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# AMERICAN CHEMICAL JOURNAL

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## METATHETIC REACTIONS BETWEEN CERTAIN SALTS IN SOLUTION IN LIQUID AMMONIA.

BY E. C. FRANKLIN AND C. A. KRAUS.

The great power of anhydrous ammonia as an electrolytic solvent, occupying as it does, of all known solvents, a position nearest to water in its power of dissociation<sup>1</sup> and in its capacity as a general solvent,<sup>2</sup> has led the authors to inquire whether or not metathetic reactions, similar to those which take place in aqueous solutions, do not take place also in ammonia solutions. If salts in solution in ammonia are dissociated to an extent approximating the dissociation in water solutions, then salts insoluble in ammonia should be precipitated rapidly and completely when ammonia solutions of salts containing the ions necessary for the formation of such substances are brought together. That in a considerable number of cases such action takes place, is shown by the experiments described in this paper.

### *Method of Making the Tests.*

The nitrates of 16 metals, selected because of their ready solubility, together with the fact that they were at hand, were chosen to furnish the metallic ions, while the sulphide, chloride, bromide, iodide, chromate, and borate of ammonium constitute the list of salts which were used as precipitants.

<sup>1</sup> Cady : Jour. Phys. Chem., 1, 707 (1897).    <sup>2</sup> This JOURNAL, 20, 820.

The tests were made by bringing together in a small vacuum-jacketed test-tube solutions of the nitrate and of the precipitant, and observing whether or not a precipitate was formed.

### *General Results.*

*Ammonium Chloride as Precipitant* (Table I).—Most of the metals tested are precipitated as chlorides by the action of ammonium chloride. Those chlorides, which by direct experiment were found to be entirely insoluble, separate immediately and completely when the two solutions are brought together, while those which were found to be slightly, or but moderately soluble, separate slowly and incompletely from more concentrated solutions.

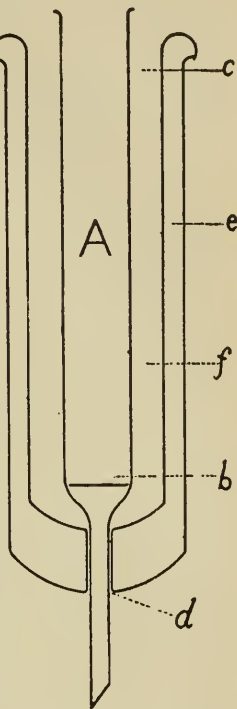
*Ammonium Bromide as Precipitant*.—Table II gives the results obtained by the use of ammonium bromide as precipitant. As was to be expected, considering the greater solubility of the bromides, these precipitates formed more slowly than the corresponding precipitates of chlorides.

*Ammonium Iodide as Precipitant* (Table III).—Corresponding with the much greater general solubility of the iodides, but two metals, barium and strontium, gave precipitates with ammonium iodide, and even these, as the crystalline nature of the precipitates indicates, are probably very slightly soluble.

*Ammonium Sulphide as Precipitant* (Table IV).—A solution of ammonium sulphide was prepared by passing washed and dried hydrogen sulphide into liquid ammonia. The gas dissolved, forming a clear, colorless solution. Ammonium sulphide was also prepared by the action of liquid anhydrous ammonia on liquid hydrogen sulphide. To the hydrogen sulphide at the temperature of the carbon dioxide and ether bath, liquid ammonia was added, with the result that immediately a mass of white solid ammonium sulphide was formed. Excess of ammonia dissolved the solid to a clear solution. On cooling the solution, saturated at the boiling temperature of ammonia, to the temperature of the carbon dioxide and ether bath, there was an abundant separation of crystals. A small quantity of these crystals, as well as a

larger quantity of the white solid, were filtered off, freed from ammonia, and transferred to a specimen tube. Although no analysis of the solid was made, there can be scarcely any doubt of its identity as ammonium sulphide.

All the metals tested, with the exception of the alkalis, gave precipitates with ammonium sulphide. Only a portion of these precipitates, however, as their most obvious property, their color, indicates, can be identical with the precipitates formed in aqueous solutions. Certainly the lead precipitate, after removing it from the solution and drying it at the laboratory temperature, is lead sulphide. The remaining black precipitates have not been studied. The precipitates formed from barium, strontium, calcium, and magnesium solutions are especially interesting for the reason that these metals in aqueous solution give no precipitates with ammonium sulphide. It is the expectation of the authors to collect and analyze these four precipitates, but up to the present, this has been accomplished in the case of but one of them, and this with not entirely satisfactory results.



*Magnesium Ammonium Sulphide,  $2\text{MgS} \cdot (\text{NH}_4)_2\text{S} \cdot x\text{NH}_3$ .*

*Preparation.*—To a Dewar test-tube containing a fairly strong solution of magnesium nitrate, an ammonia solution of ammonium sulphide was added as long as a precipitate continued to be formed. In order to separate the precipitate from the liquid, the contents of the tube were poured upon a filter, of which the following is a description. In the figure, *A* is the filtering-funnel proper, consisting simply of a thin-walled tube of the shape and size indicated, and provided with a platinum Witt filtering-plate *b*. The filtering-tube is

held in place by means of corks at *c* and *d*; *e* is a vacuum-jacketed tube. The space *f* is filled with ammonia to a convenient height.

The precipitate, after being transferred to the filter, was washed several times with fresh quantities of ammonia, the filtration being accelerated by closing the mouth of the tube by means of a cork. The pressure of the supernatant gas forces the wash-fluid through rapidly. After sufficient washing the tube was removed from the ammonia-bath, both ends were closed, one of them by means of a cork carrying a drying-tube filled with soda-lime, and the ammonia allowed to pass off at the ordinary temperature.

*Properties of the Precipitate.*—The compound was a finely crystalline, white solid, which gave off the odors of ammonia and hydrogen sulphide at the laboratory temperature. Freshly prepared, it is completely soluble in water. After standing for a short time, exposed to the air, it was no longer entirely soluble, a result due undoubtedly to the formation of magnesium hydroxide by the action of the moisture and oxygen of the air.

*Analysis of the Precipitate.*—Portions of the compound, prepared as described above, were transferred as rapidly as possible to small weighing-tubes. These were weighed and dropped into bottles containing fuming nitric acid. The sulphuric acid formed and the magnesium were determined according to the usual methods :

The following results were obtained :

	I.	II.	III.
Weight of substance,	0.1691	0.1906	0.2780
Magnesium pyrophosphate,	0.1171	0.1266	0.1793
Barium sulphate,	0.3166	0.3954	0.5828
Magnesium,	0.0231	0.0274	0.0387
Sulphur,	0.0435	0.0537	0.0794
Per cent. magnesium,	13.60	14.44	13.92
“ “ sulphur,	25.70	28.19	28.37

These determinations, made each on a different specimen of the substance, indicate in the material analyzed the presence of 2 atoms of magnesium to 3 atoms of sulphur with varying quantities of ammonia. The results obtained proba-

bly harmonize best with the assumption that the compound is a double sulphide of ammonium and magnesium, containing 2 molecules of magnesium sulphide and 1 molecule of ammonium sulphide, together with ammonia of crystallization, which, being gradually given off at temperatures above the dissociation-point of the compound, is a sufficient explanation of the variable composition as found by analysis.

The calculated percentage composition of  $2\text{MgS} \cdot (\text{NH}_4)_2\text{S} \cdot 9\text{NH}_3$  is, magnesium 14.41 per cent., sulphur 28.82 per cent., ammonia 56.16 per cent.; of  $2\text{MgS} \cdot (\text{NH}_4)_2\text{S} \cdot 10\text{NH}_3$  is, magnesium 13.71 per cent., sulphur 27.42 per cent., ammonia 58.28 per cent.

*Ammonium Chromate as Precipitant* (Table V).—Chromic acid, which presumably goes into solution as ammonium chromate, dissolves sparingly. Its solution gives precipitates with all the metals tested with the exception of lithium and sodium.

*Ammonium Borate as Precipitant* (Table VI).—Boracic acid, which in solution in ammonia presumably forms ammonium borate, is but sparingly soluble. Its solution gives precipitates with all the metals tested with the exception of lithium, sodium, and potassium.

TABLE I.

*Ammonium Chloride as Precipitant.*

Salt.	Remarks.
✓ Lithium nitrate,	precipitate, from concentrated solution.
Sodium nitrate,	no precipitate.
✓ Potassium nitrate,	precipitate, from concentrated solution.
Calcium nitrate,	precipitate, immediate.
Strontium nitrate,	" "
Barium nitrate,	" "
Magnesium nitrate,	" "
Zinc nitrate,	" "
Manganese nitrate,	" " white.
Cobalt nitrate,	" " "
Nickel nitrate,	" " light violet.
Cadmium nitrate,	" " "
Mercuric nitrate,	no precipitate.
Lead nitrate,	precipitate, from concentrated solution.
Silver nitrate,	" " " "
Copper nitrate,	precipitate, from concentrated solution, blue.

TABLE II.

*Ammonium Bromide as Precipitant.*

Salt.	Remarks.
Lithium nitrate,	precipitate, from most concentrated solutions.
Sodium nitrate,	no precipitate.
Potassium nitrate,	" "
Calcium nitrate,	precipitate, immediate.
Strontium nitrate,	" "
Barium nitrate,	" "
Magnesium nitrate,	" not immediate.
Manganese nitrate,	" immediate.
Zinc nitrate,	" not immediate.
Cobalt nitrate,	" immediate, white.
Nickel nitrate,	" " light violet.
Cadmium nitrate,	" "
Mercuric nitrate,	no precipitate.
Lead nitrate,	precipitate, from concentrated solution.
Silver nitrate,	" " " "
Copper nitrate,	precipitate, from concentrated solution, blue.

TABLE III.

*Ammonium Iodide as Precipitant.*

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	" "
Strontium nitrate,	precipitate, crystalline.
Barium nitrate,	" "
Magnesium nitrate,	no precipitate.
Zinc nitrate,	" "
Manganese nitrate,	precipitate, slowly.
Cobalt nitrate,	no precipitate.
Nickel nitrate,	" "
Cadmium nitrate,	precipitate, slowly.
Mercuric nitrate,	no precipitate.
Lead nitrate,	" "
Silver nitrate,	" "
Copper nitrate,	" "



TABLE IV.

*Ammonium Sulphide as Precipitant.*

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	precipitate, not immediate, white.
Strontium nitrate,	" immediate, white.
Barium nitrate,	" " "
Magnesium nitrate,	" not immediate, crystalline, white.
Zinc nitrate,	" immediate, white.
Manganese nitrate,	" immediate, white, dissolves on addition of water.
Cobalt nitrate,	" pinkish, on the addition of water the ppt. turns black.
Nickel nitrate,	" white, dissolves on addition of water.
Cadmium nitrate,	" white, on addition of water the precipitate becomes yellow.
Mercuric nitrate,	" immediate, black.
Lead nitrate,	" " "
Silver nitrate,	" " "
Cupric nitrate,	" yellowish brown, from concentrated solutions.
Bismuth nitrate,	" immediate, black.

TABLE V.

*Ammonium Chromate as Precipitant.*

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	precipitate, slight, flocculent.
Calcium nitrate,	" flocculent.
Strontium nitrate,	" " "
Barium nitrate,	" " "
Magnesium nitrate,	" " "
Zinc nitrate,	" " "
Manganese nitrate,	" " "
Cobalt nitrate,	" " "
Nickel nitrate,	" " "
Cadmium nitrate,	" " "
Mercuric nitrate,	" " "
Lead nitrate,	" " "
Silver nitrate,	" " "
Copper nitrate,	" " "

TABLE VI.

*Ammonium Borate as Precipitant.*

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	precipitate.
Strontium nitrate,	"
Barium nitrate,	"
Magnesium nitrate,	"
Zinc nitrate,	"
Manganese nitrate,	"
Cobalt nitrate,	"
Nickel nitrate,	"
Cadmium nitrate,	"
Mercuric nitrate,	"
Lead nitrate,	"
Silver nitrate,	"
Copper nitrate,	"

UNIVERSITY OF KANSAS, June, 1896.

## SOME PROPERTIES OF LIQUID AMMONIA.

BY E. C. FRANKLIN AND C. A. KRAUS.

The authors have been led to undertake the study of the properties of liquid ammonia in considerable detail with the object of following out, to as great an extent as possible, the manifest close relation which exists between this solvent and water. Although it has long been recognized that many derivatives of water have their analogues in certain ammonia derivatives, still the intimate relation existing between the two liquids seems never to have been fully recognized.

Water occupies an essentially unique position among the well-known solvents. Its physical properties, such as its capacity as a general solvent for salts and its power of electrolytic dissociation, its low molecular elevation constant, its high boiling-point, and its heat of fusion, heat of volatilization, critical temperature, and critical pressure, specific heat, association constant, and dielectric constant, with values so very much higher than the corresponding values for other



substances, all tend to remove it far from other solvents, and to place it in a class by itself.

From the considerations submitted below it will be recognized that, of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power of dissociating electrolytes; some salts conduct electricity even better in ammonia solution than they do in aqueous solution. It plays a part in many compounds analogous to that occupied by water in salts containing water of crystallization. Its heat of volatilization and probably its association constant are higher than those of any other liquid with the one exception of water. For a substance of such simple composition its critical temperature and critical pressure, and even its boiling-point at atmospheric pressure, are remarkably high, as is still more conspicuously true of the corresponding constants in the case of water. Its specific heat is quite as great as that of water, while its molecular elevation constant is lower than that of any other substance for which measurements have yet been made.

Ammonia differs from water in its inability to dissolve the sulphates and sulphites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances, in which latter respect it reminds one of alcohol rather than of water. The liquid does not exhibit a maximum density<sup>1</sup> above the freezing-point nor is the solid ammonia specifically lighter than the liquid at its freezing-point, as is true of solid and liquid water.

*Electrolytic Conductivity of Ammonia Solutions.*—Bleekerode,<sup>2</sup> in a paper published in 1878, on the conductivities of the liquefied halogen acids, ammonia, and certain other compounds, makes the statement that liquid ammonia is a good conductor of electricity. There can be no question, however, that he misinterpreted his results. The conductivity he

<sup>1</sup> Faraday: Watts' Dict., 2d Ed., Vol. 1, p. 183.

<sup>2</sup> Phil. Mag. (5), 5, 384 (1878), and Wied. Ann., 3, 161, (1878).

measured was undoubtedly due to a salt of sodium in solution. The passage of the current decomposed the salt, setting free metallic sodium, which, dissolving in the ammonia, gave to the solution the characteristic blue color.

Divers, in 1873, observed that the concentrated solution of ammonium nitrate in liquid ammonia, formed by the deliquescence of the salt in an atmosphere of ammonia gas, is a good electrolytic conductor.<sup>1</sup>

Led to the subject by the study of the similarity of properties and of constitution of the compounds of salts with water of crystallization to those compounds in which ammonia plays an analogous part, Cady<sup>2</sup> discovered that solutions of certain salts in liquid ammonia are conductors of electricity. He measured the conductivity of 13 salts at moderate concentration, and found that they conduct electricity in ammonia solution at  $-38^{\circ}$  almost, if not quite, as well as they do in water solution at  $18^{\circ}$ . He also found that solutions of the alkali metals conduct electricity, and with much greater facility than do salt solutions. Moreover he pointed out that these metallic solutions show no signs of polarization at the electrodes.

The authors have extended the list of determinations of the conductivity of metallic salts, and have also made measurements of the conductivity of certain organic compounds, especially the aromatic nitro-compounds, which show themselves to be good conductors in solution in ammonia. The authors have also made measurements of the increase of molecular conductivity with dilution for a number of salts, and have, further, determined the conductivity of a number of solutions at temperatures varying from  $-79^{\circ}$  up to and past the critical temperature of ammonia. The results of this work will be published in the near future.

*Metathetic Reactions in Ammonia Solutions.*—As in the case of aqueous solutions, electrical conductivity and facility of chemical reaction between substances in solution go hand in hand, so, because of the undoubtedly dissociated condition of salts dissolved in liquid ammonia, precipitates ought to be

<sup>1</sup> Proc. Roy. Soc., 21, 109 (1873).

<sup>2</sup> Jour. Phys. Chem., 1, 707 (1897).

formed instantaneously when solutions containing ions which are capable of forming salts insoluble in ammonia are brought together. That ammonia solutions do exhibit such behavior is shown by the results given in the preceding paper on "Metathetic Reactions between Certain Salts in Solution in Liquid Ammonia."

*Ammonia of Crystallization and Ammonia of Constitution.*—The authors have up to the present added but one compound to the long list of substances formed by the direct addition of ammonia to many of the metallic salts. Leaving out of consideration at the present time the very great number of such compounds, it will be sufficient to mention the early observations of Divers,<sup>1</sup> who considers the ammonia in the liquid formed by the action of ammonia on ammonium nitrate to be entirely analogous in function to the water absorbed, for instance, by calcium chloride; to the ammonia addition-products described by Joannis,<sup>2</sup> Jarry,<sup>3</sup> Bonnefoi,<sup>4</sup> formed by the action of liquid ammonia on the salts, and to the slaking phenomena attendant upon the action of liquid ammonia on certain halogen salts first described by Gore,<sup>5</sup> and also observed by the authors in their investigations on liquid ammonia as a solvent.<sup>6</sup>

*Specific Heat of Ammonia.*—The specific heat of liquid ammonia has been calculated from thermodynamic data by Zeuner, Ledoux, and Wood. It has also been made the subject of experimental investigation by Regnault, Von Strombeck,<sup>7</sup> Lüdeking and Starr,<sup>8</sup> and Elleau and Ennis.<sup>9</sup> For the experimentally determined values, Von Strombeck found 1.22876 at 45°, Lüdeking and Starr 0.8857 at 40°, and Elleau and Ennis 1.021 at 10°. Calculated from Professor Wood's formulæ<sup>10</sup> the values 0.98 to 1.14 at 10° are obtained.

*Boiling-point of Ammonia.*<sup>11</sup>—While the boiling-point of am-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Compt. rend.*, **112**, 337 (1891).

<sup>3</sup> *Ibid.*, **124**, 288 and 963 (1897); **126**, 1138 (1898).

<sup>4</sup> *Ibid.*, **124**, 771 (1897).

<sup>5</sup> *Proc. Roy. Soc.*, **20**, 441 (1872).

<sup>6</sup> *This JOURNAL*, **20**, 820.

<sup>7</sup> *Jour. Frank. Inst.*, **130**, 467 (1890).

<sup>8</sup> *Am. J. Sci.* (3), **45**, 200. (1893).

<sup>9</sup> *Jour. Frank. Inst.*, **145**, 189 (1898).

<sup>10</sup> *Thermodynamics*, p. 325; *Trans. A. I. M. E.*, **12**, 136, and **10**, 645.

<sup>11</sup> Regnault gives 38°.5; Loir and Drion, 35°.7; and Bunsen, 33°.7 as the boiling-point of ammonia. *Watts' Dict. Chem.*, 2d Ed., Vol. 1, p. 183; Supplement, Vol. 6, p. 102. Joannis gives the boiling-point at 38°.2, *Compt. rend.*, **115**, 820 (1893).

monia is much below that of water, still it is high when compared with the boiling-points of other simple compounds of elements with low atomic weights. The boiling-points of hydrogen sulphide, hydrogen selenide, the halogen acids, methane, ethylene, acetylene, phosphine, and even arsine, stibine, and hydrogen telluride, are all below, and some of them far below the boiling-point of ammonia. As is the boiling-point of water, so is the boiling-point of ammonia, although to a less extent, abnormally high.

*Heat of Fusion.*—No determinations of the heat of fusion of solid ammonia have yet been made.

*Heat of Volatilization of Ammonia.*—With the exception of some preliminary measurements by the authors, no direct determinations of the heat of volatilization of ammonia at its boiling-point at atmospheric pressure have yet been made. Regnault's value<sup>1</sup> of 294.21 is the result of measurements made at 7°.8. Von Strombeck<sup>2</sup> obtained 292.4 as the result of measurements made at 14° to 18°. As preliminary results, the authors have obtained 326 to 332 as the heat of volatilization of ammonia at its boiling-point. A description of the method by which these measurements were made, together with the final values, will be published in a later paper.

The heat of volatilization of ammonia at any required temperature may also be calculated from thermodynamic formulæ. From a formula used by engineers in calculating the capacities of refrigerating-plants,  $h_e = 300 - 0.8t$ ,<sup>3</sup> the value for the heat of volatilization of ammonia at  $-38^\circ$  is calculated to be 330 calories.

Another formula given by Professor Wood,<sup>4</sup>  $h_e = 555.5 - 0.613T - 0.000219T$ , in which English heat units and Fahrenheit temperatures are to be understood, if used for calculating the heat of volatilization of ammonia, gives a value of 321 cal. at  $-38^\circ$  C.

The heat of volatilization of a liquid may also be calculated by means of the law of Trouton,<sup>5</sup> according to which the molecular heats of volatilization of closely related substances

<sup>1</sup> Landolt und Börnstein, *Physikalisch-chemische Tabellen*.

<sup>2</sup> *Loc. cit.*, p. 472.

<sup>4</sup> *Thermodynamics*, p. 332.

<sup>3</sup> Peabody : *Thermodynamics*, p. 459.

<sup>5</sup> *Phil. Mag.* (5), 18, 54 (1888).

are directly proportional to their absolute boiling-points. In the expression for Trouton's law  $\lambda M/T = k$ , in which  $\lambda$  is the heat of volatilization,  $M$  the molecular weight, and  $T$  the absolute boiling-point, the values of  $k$ , in the case of water, methyl alcohol, ethyl alcohol, and amyl alcohol are respectively 25.9, 25.7, 26.3, and 26.2. If we are justified in assuming that ammonia is closely related to water, then by substituting the values,  $k = 25.9$ ,  $T = 235$ , and  $M = 17$ , in the formula  $\lambda = kT/M$ , the latent heat of volatilization of ammonia is calculated to be 358 calories.

These values, while not in as good accord as might be wished, still agree in showing that the heat of volatilization of liquid ammonia, of all known liquids, is second only to water.

*Molecular Elevation Constant of Ammonia.*—Other than by direct experimental determination, the molecular elevation constant of a liquid may be calculated by means of the formula of Van't Hoff, provided the heat of volatilization and the boiling-point of the liquid are known. Several approximate values for the heat of volatilization of ammonia are given above, which by substitution in the formula,  $k = 0.02T^2/\lambda$ , yield the values given below for the molecular elevation. Values for the molecular elevation of the boiling-point, experimentally determined for a number of substances,<sup>1</sup> are also included in the table.

	$h_e$ .	$k$ .
Peabody's formula,	329	3.35
Wood's        "	321	3.44
Trouton's     "	358	3.09
$H_e$ direct,	329	3.36
Water,		3.4
Ethyl alcohol,		3.4
Propyl       "		3.4 to 2.7
Pyridine,		3.3 to 1.8
Aniline,		3.9 to 3.1
Potassium iodide,		3.2 to 5.9

Certainly the molecular elevation of the boiling-point of ammonia is smaller than that of any other solvent for which measurements have yet been made.

<sup>1</sup> This JOURNAL, 20, 836.



*The Dielectric Constant of Ammonia.*—This constant has recently been measured by Dr. H. M. Goodwin,<sup>1</sup> of the Massachusetts Institute of Technology, who finds a value of about 20. These measurements, if Nernst's hypothesis holds true, show that the dissociation of salts in liquid ammonia may not be as great as we had supposed.

*Molecular Association of Ammonia.*—Some indication of the degree of association of a liquid may be arrived at by the application of the methods given by J. Traube in a recent paper.<sup>2</sup>

For liquid ammonia we have calculated the values,  $190_{-38}$ , 23.9 and 0.00079, for  $x_2$ ,  $\frac{M\lambda}{T}$  and  $\frac{M}{m} \frac{T' - T}{pT}$ , respectively,<sup>3</sup> results which place liquid ammonia among the associated liquids along with water and the alcohols.

If 55.90, the approximate molecular heat of volatilization of ammonia, be substituted in place of an incorrect value used in a table recently published by Vaubel,<sup>4</sup> then the association constant of liquid ammonia approaches that of water and excels that of the alcohols instead of indicating ammonia to be a non-associated liquid.

UNIVERSITY OF KANSAS,  
September, 1898.

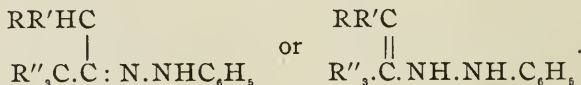
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Contributions from the Laboratory of General Chemistry, University of Michigan.

## ON THE CONSTITUTION OF THE PHENYLHYDRAZONES.

BY PAUL C. FREER.

Two possible constitutions can be assigned to the compounds of phenylhydrazine with ketones and aldehydes—the *hydrazone* or the *hydrazo* structure :



Attention has been called by others<sup>5</sup> to the fact that certain

<sup>1</sup> Paper read before Sec. B, American Association for the Advancement of Science, 1898.

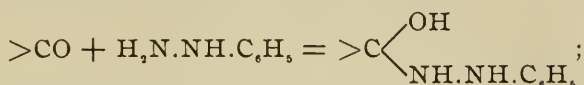
<sup>2</sup> Ber. d. chem. Ges., **30**, 265 (1897).

<sup>3</sup> Loc. cit., p. 273.

<sup>4</sup> Jour. prakt. Chem. (5), **57**, 351 (1898).

<sup>5</sup> V. Meyer und Jacobson: Lehrbuch II, 326; Nef: Ann. Chem. (Liebig), **270**, 289; **300**, 319; **280**, 294.

ketones react with phenylhydrazine by addition, first producing the hydrazone hydrates :



but all such bodies have heretofore been either the anilides or methyl amides of ketone acids, *i. e.*, the anilides of mesoxalic, pyruvic, and benzoylpyruvic acids, and the methylamide of benzoylpyruvic acid. No other ketones have as yet given similar hydrates as, presumably, the compounds discovered by Wislicenus<sup>1</sup> are more of the nature of salts. I have noticed, however, that if the absolute ethereal solutions of aldehyde, methylethylketone, or similar aliphatic compounds, are cooled to  $-20^\circ$ , and then mixed with absolutely pure, crystallized phenylhydrazine, a crystalline precipitate is at once formed, only to dissolve and disappear on standing for some time, while changing to the hydrazone. In all probability these precipitates consist of hydrazone hydrates, but whether this be true or not, I have no doubt that, in all cases in which hydrazones are formed, there is a previous addition of phenylhydrazine to the ketone or aldehyde, followed by a separation of water. This assumption is in entire accord with what we know in regard to the behavior of these bodies toward other reagents, such as ammonia or hydrocyanic acid, to use the most familiar examples. In these instances the hydrate happens, however, to be stable and consequently easily isolated. Once the addition of phenylhydrazine has taken place, it is obviously conceivable that the separation of water should take place in the one direction, in order to produce the hydrazone, or in the other, to form the hydrazo body, and, of course, it is also possible that representatives of both classes may be produced at the same time.

In considering the constitution of the phenylhydrazones, one fact is at once apparent : certain members of this class of bodies, such as the derivatives of acetone, methylethylketone, other aliphatic ketones, and acetophenone, are readily oxidized in the air, changing to non-crystallizable tars and at the

<sup>1</sup> Ber. d. chem. Ges., 24, 2008.

same time giving off large quantities of gas, while others, such as pyruvic or acetoaceticether phenylhydrazones, are perfectly stable or at least change to other bodies which are *not* oxidation-products.<sup>1</sup> In a former article I called attention to this behavior<sup>2</sup> and suggested then that possibly this difference in behavior might be due to a difference in constitution. It is certain that this contrast would, in the past, have become a subject of investigation if it had been possible to isolate the products produced by oxidizing the former class of bodies but, in all probability, the attempts proved failures because of the difficulty of obtaining pure, crystallized substances; for I have discovered that these oxidation-products, when isolated, are extremely unstable. According to our present views it is generally accepted as true that the hydrazo structure  $R.NH.NH.R'$  must be assigned to compounds which are converted into azo bodies by oxidation, especially if the former can readily be reproduced from the latter by reduction. In the course of this work I have found that acetone-*p*-bromophenylhydrazone, when carefully subjected to the action of air, is quantitatively changed to a red, explosive azo body, and that sodium amalgam as readily reverses the process, leaving the original substance as a final product. The same change can be accomplished in the same way with acetophenone-*p*-bromophenylhydrazone and with acetophenonephenylhydrazone, although in the case of the last body mentioned, the product is not crystallizable. Reduction accomplishes the same end with these compounds as it does with the acetone derivative. All of these azo bodies, in conformity with the behavior of azobenzene itself, form crystalline perbromides, which can also be reduced to the original hydrazones. The perbromides have such a characteristic appearance and undergo such typical changes on heating or on boiling with alcohol, that their formation can properly be used to identify the azo bodies themselves. Judging by these reactions, the above-mentioned hydrazones have the following general structural formula :

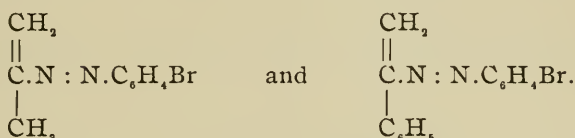
<sup>1</sup> Acetoaceticether phenylhydrazone changing to 1-phenyl-3-methyl-5-pyrazolone.

<sup>2</sup> Ann. Chem. (Liebig), 283, 391.





because the corresponding azo bodies have the following constitution :



In order to secure further proof that I really had to deal with substances containing the azo grouping, I investigated the oxidation of benzoyl-*p*-bromphenylhydrazine for purposes of comparison. Fischer<sup>1</sup> had already undertaken similar work with benzoylphenylhydrazine, obtaining, however, only an oil on oxidizing with yellow oxide of mercury. He was unable to crystallize or purify the body, but reconverted it into the mother-substance by reduction. I secured better results with the *p*-brominated compound, for the latter, when treated with the above-mentioned reagent, is readily changed into a fine, red, crystalline body which resembles those obtained from the hydrazones in every particular except that it is more stable; bromine converts the red crystals into a garnet-colored perbromide, which decomposes on boiling with alcohol, into nitrogen, benzoic ether, and brominated phenols in a manner exactly analogous to the behavior of the perbromides obtained from the oxidation-products of the hydrazones.

As there seems to be no doubt that many phenylhydrazones are readily oxidized to azo bodies, the question at once arises whether this reaction can be looked upon as absolute proof of the hydrazostructure of the original substances, and the answer is to be obtained by determining whether other changes which they can undergo, conform equally well with this view. As a result of this consideration I undertook the investigation of the action of benzoyl chloride on the substances in question. If

<sup>1</sup> Ann. Chem. (Liebig), 190, 126.

acetonephenylhydrazone is dissolved in cold toluene and then mixed with benzoyl chloride, a slow reaction sets in and an insoluble syrup, in addition to the hydrochloride of the base, is produced. This syrup is readily converted into acetone and dibenzoylphenylhydrazine when treated with a dilute alcoholic solution of hydrochloric acid, so that a body which contains two benzoyl groups to each molecule has been formed, because dibenzoylphenylhydrazine but not a trace of the monobenzoyl compound is separated from it. Acetophenonephenylhydrazone behaves in the same way, dibenzoylphenylhydrazine, but none of the mono compound, being produced.<sup>1</sup>

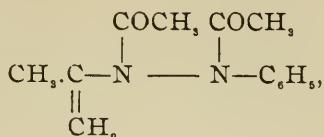
In contrast to the above, the phenylhydrazones of pyruvic ester and of benzophenone, both of them non-oxidizable and unquestionably true hydrazones, are not acted on by benzoyl chloride even when heated to  $140^{\circ}$ ; indeed, the temperature reaches  $165^{\circ}$ – $180^{\circ}$  before a change sets in, and then there results a mixture of mono- and dibenzoylphenylhydrazine. So far, then, there seems to be a marked contrast between those bodies which can be oxidized to substances with azo structure and those which cannot. Overton<sup>2</sup> mentions a case in which acetyl chloride acts upon anisylphenylketonephenylhydrazone and describes what must be considered as an addition-product. This substance is a horn-like mass which absorbs moisture from the air, decomposing with water to form anisylphenylketone and monoacetylphenylhydrazine, again demonstrating a difference between the behavior of a true hydrazone and one of the class of bodies under consideration. In only very few instances have crystalline acyl substitution-products been obtained from phenylhydrazine derivatives of ketones and of the small number of bodies which have been so classed, one, at least, has proved to be of an entirely different structure.

Nef<sup>3</sup> studied the action of acetyl chloride on the hydrazone of acetoacetic ester and obtained what he considered to be a body of the following structure :

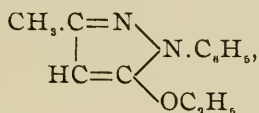
<sup>1</sup>  $\beta$ -Benzoinphenylhydrazone also reacts with benzoyl chloride but in an entirely different manner. This will be discussed further on.

<sup>2</sup> Ber. d. chem. Ges., 26, 23.

<sup>3</sup> Ann. Chem. (Liebig), 266, 75.



and looked upon its formation as a further proof of the hydrazo formula of that substance. In the course of my work, however, it was demonstrated that the result of this reaction has the composition represented by  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}$ ,<sup>1</sup> and Walker<sup>2</sup> rendered the following constitution probable :



so that this presumed diacetyl substitution-product can no longer be classed as such. The only definitely described bodies of this class are therefore the pentabenzoyl derivative of phloroglucinphenylhydrazone,<sup>3</sup> the monoacetylpyruvic aldehydehydrazone of Japp and Klingemann,<sup>4</sup> obtained by the action of acetic anhydride on pyruvic aldehydehydrazone and a tetrabenzoyl body derived from succinylsuccinicester phenylhydrazone which is very briefly mentioned by Nef.<sup>5</sup> In the first case, Von Baeyer and Kochendorfer have shown that the phenylhydrazone of phloroglucin is unquestionably a hydrazo body, for they oxidized it to the corresponding azo derivative, just as is the case with the bodies described by me ; pyruvic aldehydehydrazone, on the other hand, has a different structure, and yields a monoacetyl derivative. So far as our experience reaches, therefore, it is evident that those hydrazones which can be changed to azo bodies react with benzoyl chloride, either to give non-crystallizable bodies from which dibenzoylphenylhydrazine can be obtained or they give, as is shown in one instance, stable derivatives in which acyl groups are substituted for both hydrazo hydrogen atoms. The true hydrazones, on the other hand, which, of course, cannot be oxidized to bodies with the azo structure, are either not acted on

<sup>1</sup> This JOURNAL, 14, 487.

<sup>2</sup> *Ibid.*, 15, 584.

<sup>3</sup> Ber. d. chem. Ges., 22, 2192.

<sup>4</sup> Ann. Chem. (Liebig), 247, 196.

<sup>5</sup> *Ibid.*, 266, 76.

at all by acyl chlorides or they are converted into monoacylated derivatives, or into monosubstituted phenylhydrazines. These considerations furnish a further proof of the hydrazo nature of acetonephenylhydrazone and of acetophenonephenylhydrazone.

The majority of phenylhydrazones cannot be benzoylated according to the Baumann-Schotten method. Acetone-*p*-bromphenylhydrazone, acetophenone-*p*-bromphenylhydrazone, pyruvic phenylhydrazone did not react; acetoaceticester phenylhydrazone was saponified, yielding phenylmethylpyrazolone and non-crystallizable tars. It seems to be generally believed that phenylhydrazones should all react readily with acyl chlorides in such a way that the hydrogen atoms attached to nitrogen can be substituted. From what has gone before, however, it is evident that this is the case only in certain instances.

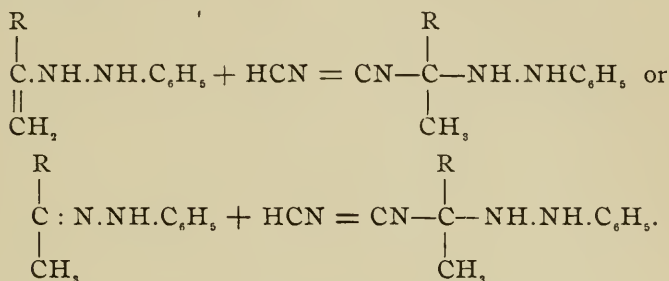
It would seem probable that these phenylhydrazine derivatives of aldehydes or ketones which can be readily converted into azo bodies should also react with benzoic aldehyde to form hydrazoïnes, just as hydrazobenzene itself does.<sup>1</sup> This is not the case, however, at least with acetonephenylhydrazone, for the latter body is quantitatively converted into benzalphenylhydrazine and acetone, even in the cold. Phthalic anhydride, on gentle heating, acts in the same way, phthalylphenylhydrazone being produced, but these negative results show how readily this phenylhydrazone is decomposed, a fact which again points to its hydrazo structure.

An unbiased opinion as to the structure of the bodies under discussion cannot be formed, however, unless the addition-reactions of Miller and Plöchl<sup>2</sup> with Schiff's bases and the phenylhydrazones of aldehydes and ketones are considered. These investigators demonstrated that hydrocyanic acid readily adds itself to the phenylhydrazones derived from aliphatic ketones or aldehydes, but that it is indifferent toward those of the aromatic or semiaromatic series. Pyruvic hydrazone forms an exception to the rule. Now it is apparent that

<sup>1</sup> Cornelius and Homolka : Ber. d. chem. Ges., 19, 2239.

<sup>2</sup> *Ibid.*, 25, 2020; 27, 1281.

such additions could take place regardless of whether the unsaturated linking is between two carbon atoms or between a carbon and a nitrogen atom, for in either case the same product would result.<sup>1</sup>



It has been shown, so far as the investigation has been extended, that all aliphatic hydrazones (also acetone-*p*-bromophenylhydrazone, which yields an azo body) take up hydrocyanic acid with the exception of pyruvic acid phenylhydrazone, and the latter body, as will be shown below, does not possess the hydrazo structure. The conclusion might be drawn from these facts that pyruvic phenylhydrazone does not possess the same constitution as the others, but then we find that acetophenonephenylhydrazone—which undoubtedly yields an azo body—is also incapable of adding hydrocyanic acid, so that we are forced to the conclusion that Miller and Plöchl's reactions can prove neither the one nor the other constitution.

The present condition of our views as to structural chemistry, therefore, forces us to the belief that those hydrazones which can be readily oxidized to azo bodies, and react with benzoyl chloride in the manner outlined above, really have the hydrazo structure, for the oxidation of a body of the for-

mula,  $\begin{array}{c} \text{R} \\ | \\ \text{C} : \text{N.NHC}_6\text{H}_5 \\ | \\ \text{CH}_3 \end{array}$ , to an individual containing azo nitro-

gen although conceivable, is scarcely probable.

In view of the above considerations we should, however, be

<sup>1</sup> Bredt and Kallen (Ann. Chem. (Liebig), 293, 238) have demonstrated that hydrocyanic acid can add itself to the unsaturated linking of a pair of carbon atoms.



able to obtain substances belonging to both classes from the interaction between one and the same ketone or aldehyde and phenylhydrazine. This seems to be the case with the benzoïnphenylhydrazones. Smith and Ransom<sup>1</sup> have proved the existence of two benzoïnphenylhydrazones, one melting at 106° and the other at 159°, and naturally looked upon the same as geometric isomers. On applying the methods used in this investigation, however, it could readily be shown that these bodies are fundamentally different in their chemical behavior. When the low-melting substance is treated with benzoyl chloride in ethereal solution it undergoes a remarkable change into a new body, entirely different from either the  $\alpha$ - or  $\beta$ -phenylhydrazones, but it nevertheless has the same composition and molecular weight, and consequently is an isomer. There are, therefore, in reality three benzoïnphenylhydrazones.  $\beta$ -Benzoïnphenylhydrazone, dissolved in ether and saturated with gaseous nitrogen trioxide, yields a garnet-colored, azo-like body which, however, is in reality an addition-product of the oxide and the presumed azo derivative. This addition-product gives a perbromide, just as the previously described simple substances do, the crystals of which have the same appearance and decompose in the same way.  $\alpha$ -Benzoïnphenylhydrazone is not attacked by benzoyl chloride in the cold, and with nitrogen trioxide it yields a white crystalline precipitate which gives a body melting at 212° on treatment with alkalis. The latter is probably the tetrazone.<sup>2</sup> The new isomer does not react with benzoyl chloride, and is changed but little, if at all, by nitrogen trioxide. It is not, therefore, difficult to select the hydrazo body from the three hydrazones of benzoïn—the substance which is easily changed by benzoyl chloride and is so readily attacked by the oxide of nitrogen is undoubtedly the one. It is not unlikely that similar relationships exist between the acetaldehydrazones of Fischer,<sup>3</sup> but the investigation in this instance is beset with greater difficulty, owing to the fact that one body is converted into the other with such readiness. Both the  $\alpha$ - and  $\beta$ -hy-

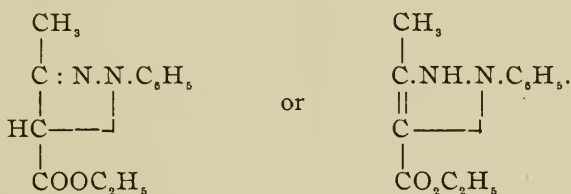
<sup>1</sup> This JOURNAL, 16, 108.

<sup>2</sup> Pechmann : Ber. d. chem. Ges., 26, 1045.

<sup>3</sup> Ber. d. chem. Ges., 29, 793.

drazones behave alike toward nitrogen trioxide, yielding a white, crystalline, and extremely explosive product, probably the nitroso derivative. If the latter is shaken with alkalis, it forms a yellow body, similar to that obtained from  $\beta$ -benzoïnphenylhydrazone, and this also forms a perbromide.  $\beta$ -Acetaldehydhydrazone is readily oxidized by yellow oxide of mercury, but the resulting substance, probably an azo body, is an oil, which, however, readily yields a perbromide; the  $\alpha$ -phenylhydrazone is indifferent when treated with mercuric oxide. It does not seem likely, in view of the above, that the distinction between these two phenylhydrazones is one of geometric isomerism.

So far as I know, there is only one body directly derived by oxidizing an aliphatic phenylhydrazone, which is supposed to have the azo structure described in chemical literature. Nef<sup>1</sup> has shown that acetoaceticester phenylhydrazone can be oxidized by mercuric oxide to a red body, melting at  $47^\circ$ , which is generally considered to be benzeneazo- $\beta$ -oxycrotonic ester, but it is also true that the same substance is produced by the action of phenylhydrazine on  $\alpha$ -chloracetoacetic ester.<sup>2</sup> If we take the first formation alone into consideration, the azo structure would scarcely be open to question but, unless we accept the view that an atomic rearrangement takes place, it is impossible to obtain an azo body according to the second method; indeed, according to that synthesis one of the two following structural formulæ must result:

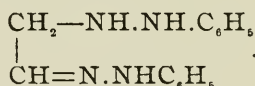


An investigation into the chemical behavior of benzeneazo- $\beta$ -oxycrotonic ester increases the doubt as to its azo structure and renders the other formulæ more probable. The body does not give a perbromide, as is the case with analogous substances, but, on the other hand, bromine seems to cause

<sup>1</sup> Ann. Chem. (Liebig), **266**, 74.

<sup>2</sup> Bender: Ber. d. chem. Ges., **20**, 2747.

nearly complete decomposition into tarry products, from which but one pure body, described below, can be isolated. Reduction does not reproduce the mother-substance but, in place of the latter, phenylmethylpyrazolone and bisphenylmethylpyrazolone result. The substance in question melts quietly, without the evolution of a gas and, as Thiele<sup>1</sup> has demonstrated with the azo body obtained from hydrazoisobutyric acid and similar substances, and as is shown by the study of my semi-aromatic azo derivatives, all such bodies decompose and yield their nitrogen contents on being heated to a temperature slightly above their melting-points. Experiments with the object of obtaining substances similar to benzeneazo- $\beta$ -oxycrotonic ester, by the method employed by Bender, have not succeeded in producing a parallel case. Hess<sup>2</sup> studied the action of bromacetophenone on phenylhydrazine and obtained a yellow, crystalline body. If this had the azo structure it would closely resemble the substance produced by me from acetophenone-*p*-bromphenylhydrazone, but investigation showed that its properties differed entirely from those of the latter, and that its molecular weight was greater than is represented by the formula  $C_{14}H_{12}N_2$ . Chloraldehyde hydrate simply yields a substance of the composition :



Chloracetone produces much more complicated bodies, neither do brom- or chlorlævulinic ester lead to the desired result.<sup>3</sup> The reaction with  $\alpha$ -chloracetoacetic ester is, therefore, entirely different from those observed with the other  $\alpha$ -halogen-substituted ketones, and, therefore, from lack of material for comparison, its azo structure cannot positively be denied ; nevertheless, its formation and its behavior point strongly toward the constitution given above, while, at the same time, the azo formula becomes doubtful.

<sup>1</sup> Ann. Chem. (Liebig), **290**, 33.

<sup>2</sup> *Ibid.*, **232**, 234.

<sup>3</sup> Bender: Ber. d. chem. Ges., **21**, 2492.



## EXPERIMENTAL DETAILS.

*The Action of Benzoyl Chloride on Acetonephenylhydrazone.*

10.9 grams of pure acetonephenylhydrazone were dissolved in 100 cc. of absolute ether, an excess of precipitated chalk added, and then the calculated quantity of benzoyl chloride poured in; the whole was then allowed to stand for one week at winter temperature, care being taken to shake frequently. At the expiration of this time the odor of benzoyl chloride was nearly gone, so that the precipitate was filtered, washed with water, and finally with dilute hydrochloric acid to remove the chalk, then dried and recrystallized from alcohol. It melted at  $178^{\circ}$ , and was dibenzoylphenylhydrazine. The filtrate, which had assumed a dark-red color, was evaporated *in vacuo*, leaving a dark oil, which gradually deposited a further quantity of dibenzoylphenylhydrazine. No other product could be isolated. In order, if possible, to separate the supposed addition-product, the reaction was repeated without the chalk, and with the substitution of toluene for ether as a solvent.

57 grams acetonephenylhydrazone were dissolved in 100 cc. toluene and then 15 grams ( $\frac{1}{3}$  of the calculated quantity) of benzoyl chloride added, the whole being allowed to stand at ordinary temperature. At the expiration of twelve hours the solution had separated into two parts, an upper layer consisting of toluene, colored red, and a lower thick syrup, both sections being permeated with white crystals.

A. *The Crystalline Body*.—Recrystallized from acetone, this body separates in white plates with a luster resembling mother-of-pearl. It is soluble in water, and the addition of alkalies to the solution so produced precipitates an oil which does not reduce Fehling's solution. An analysis showed 19.15 per cent. chlorine to be present; calculated for the hydrochloride of acetonephenylhydrazone, 19.20 per cent. Acetonephenylhydrazone hydrochloride was prepared in ethereal solution by the action of hydrochloric acid gas and was shown to be identical with the substance under investigation.

B. *The Toluene Solution*.—This contained nothing but unchanged material and a trace of acetone.

C. *The Syrup*.—The syrup contains a large proportion of chlorine, and no method was found which could induce it to crystallize. It was consequently covered with pure ether, allowed to stand, the ether poured off, and this process repeated until all toluene, as well as any acetone which might possibly be present, was washed out. It was then covered with dilute pure alcohol to which a few drops of hydrochloric acid had been added, and allowed to stand. After a short time the whole nearly solidified to a crystalline mass of dibenzoylphenylhydrazine. A further portion of the syrup was covered with absolute alcohol and left over night, by which time some crystals of dibenzoylphenylhydrazine had separated. These were filtered and then 5 cc. of dilute hydrochloric acid were added to the filtrate, when a further separation of the same body took place. The latter was again separated, and then the brown mother-liquors were distilled, all that went over below  $80^{\circ}$  being collected. This portion was saturated with potassium carbonate, the supernatant fluid collected, fractionated, dried with fused sodium sulphate, and finally mixed with a concentrated solution of sodium bisulphite, whereupon the whole solidified to the characteristic flakes of acetone-sodium bisulphite. Pure acetone was then isolated from the latter in the usual manner. The syrup which is insoluble in toluene is, therefore, most probably a dibenzoyl compound of acetonephenylhydrazone, which is decomposed into acetone and dibenzoylphenylhydrazine by means of alcoholic hydrochloric acid. No monobenzoylphenylhydrazine could be isolated. The mother-liquors invariably contain thick, non-crystallizable tar, in addition to the above. I was unable to obtain anything definite by employing a mixture of benzoyl chloride, sodium and phenylhydrazine, in the presence of absolute ether.

*The Action of Benzoyl Chloride on Acetophenonephenylhydrazone.*

This reaction takes the same course as that just described as taking place with the corresponding acetone compound. 6.3 grams of acetophenonephenylhydrazone were dissolved in benzene, and then 3.4 grams of benzoyl chloride added,

the whole being constantly stirred. The change is complete after forty-eight hours. The solvent was then evaporated in a vacuum, the remainder being a thick, black oil, permeated with a few crystals which proved to be the hydrochloride of acetophenonephenylhydrazone. The oil was covered with a solution of hydrochloric acid in dilute alcohol, and after a short time crystals of dibenzoylphenylhydrazine formed, the mother-liquors containing acetophenone.

Benzoic anhydride (5.4 grams) and acetophenonephenylhydrazone (5 grams) were sealed in a tube and heated for eight hours at 100°. A semi-solid mass remained. On cooling, this was extracted with ether, the solvent leaving white crystals of dibenzoylphenylhydrazine. The ethereal solution contained benzoic acid and acetophenone. Benzoic anhydride, therefore, behaves as does benzoyl chloride; it separates the hydrazone into dibenzoylphenylhydrazine and acetophenone, while, at the same time, it is itself converted into benzoic acid. Attempts to benzoylate acetone-*p*-bromophenylhydrazone and acetophenonephenylhydrazone in the presence of caustic soda, according to the method of Baumann and Schotten, were failures because the substances in question were not attacked.

*The Action of Benzoic Aldehyde and of Phthalic Anhydride on Acetonephenylhydrazone.*

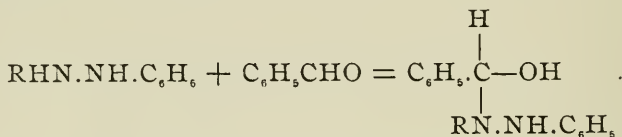
Acetonephenylhydrazone (6 gràms) and benzoic aldehyde (5.4 grams) were dissolved in alcohol, mixed, and allowed to stand over night. At the expiration of this time a large quantity of crystals had separated. These were filtered and recrystallized, and proved to be benzalphenylhydrazone.

Acetonephenylhydrazone (6 grams) was heated over a free flame with the calculated amount of phthalic anhydride, until reaction began. The whole was then set aside and warmed from time to time until the reaction was completed. There remained a transparent, semisolid mass, which solidified when rubbed under water. The product was finally crystallized from alcohol and, when pure, melted at 149°, which shows that it is phthalylphenylhydrazone.

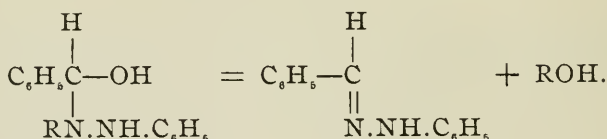
These two reactions show the ease with which acetonephenylhydrazone is separated into its component parts, and such a behavior is to be expected of a hydrazo body having

the structure  $\begin{array}{c} \text{CH}_3 \\ || \\ \text{C.NH.NHC}_6\text{H}_5 \\ | \\ \text{CH}_3 \end{array}$ , but would scarcely be pre-

dicted of a hydrazone. It is scarcely to be doubted, as was mentioned in the introduction, that the hydrazones are produced from the hydrates, owing to a separation of water from the latter bodies, and exactly the same change takes place when benzoic aldehyde acts upon acetonephenylhydrazone, the structure of the latter still permitting it to act much in the same manner as free phenylhydrazine. The first change is therefore the addition of benzaldehyde to form the hydrate, as follows :



In the next stage of the reaction isoacetone separates, instead of water, as is the case with the phenylhydrazone hydrates :



Finally, the isoacetone changes to ordinary acetone. The same series of reactions undoubtedly take place in the case of phthalic anhydride.

*The Action of Bromine on Acetonephenylhydrazone:—  
Acetone-p-bromphenylhydrazone.*

54 grams of pure, crystallized<sup>1</sup> acetonephenylhydrazone

<sup>1</sup> If pure acetone, in ethereal solution, is treated with pure, recrystallized phenylhydrazine and the ether then evaporated *in vacuo*, the phenylhydrazone separates in crystalline form. Recrystallized from ligroin it melts at 31°-32°. See also Arnold : Ber. d.chem. Ges., 30, 1015.

were dissolved in 300 cc. of absolute ether, cooled with snow and salt, and then 58.3 grams of bromine gradually dropped in, care being taken to stir vigorously during the entire operation, and to exclude the air by means of carbon dioxide. The color of the bromine disappeared as soon as the drops came in contact with the liquid, and at the same time a white, crystalline substance began to separate. This latter was the hydrobromide of acetone-*p*-bromphenylhydrazone. When all of the halogen had been added, the whole was allowed to stand an hour longer in the freezing-mixture, after which time the precipitate was filtered in an atmosphere of carbon dioxide. This precaution is necessary because the white crystals soon become violet in the air, finally changing to a sticky tar. The product was thoroughly washed with ether, dried in a current of the same gas, and then covered with an excess of dilute caustic potash, by which means it was changed to a somewhat yellow mass of sandy crystals. The latter are washed with water until they are entirely freed from alkali, pressed, and then dried on a porous plate in an atmosphere of carbon dioxide. They are finally purified by repeated recrystallization from ligroïn. They consist of white, shiny plates melting at 98°-99°.<sup>1</sup> Analysis showed 34.7 per cent. bromine; calculated 35.3 per cent. If the ethereal mother-liquors are allowed to stand in the cold, a further separation of the hydrobromide of acetone-*p*-bromphenylhydrazone takes place. The yield is almost quantitative, only the very last residues yielding a little tarry substance and having the odor of bromine substitution-products of acetone. Any doubt as to the identity of the body produced is dispelled by the following experiments:

4 grams of the pure crystals were boiled with hydrochloric acid in a vessel connected with an inverted condenser for one-half hour; the solution was then rendered alkaline and the white precipitate filtered, dried, and weighed, the quantity being 3 grams (calculated 3.3 grams). The body produced crystallizes in long needles from hot water and has a melting-

<sup>1</sup> Absolutely pure acetone-*p*-bromphenylhydrazone melts at 98°-99° (uncorr.). The highest melting-point previously observed is that observed by Bamberger. This was 95° (Ber. d. chem. Ges., 30, 217).



point of  $105^{\circ}$ – $106^{\circ}$ . Comparison with a preparation obtained in a different way, proved it to be *p*-bromphenylhydrazine. This method is the best, so far as I know, for preparing the latter substance.

A comparison of acetone-*p*-bromphenylhydrazone, formed by direct bromination, with a sample produced synthetically, also confirmed its identity.

This reaction is a general one with hydrazones, the only difference lying in the slight variation of detail necessary in each instance.

*Acetophenone-p-bromphenylhydrazone.*

24 grams of acetophenonephenylhydrazone were dissolved in 200 cc. of dry ether, cooled in a freezing-mixture, and 17.6 grams of bromine were gradually added, the liquid being meanwhile thoroughly stirred. A white, sticky mass begins to separate at once, and if a sample of this is spread on a porous plate it gradually changes to crystals which separate from hot water in needles melting at  $106^{\circ}$ , and are therefore *p*-bromphenylhydrazine. In order to avoid the formation of this body, the whole solution, including the precipitate, was thoroughly shaken with an excess of 10 per cent. caustic potash, as soon as all of the bromine had been added. It was then dried over fused sodium sulphate and the ether distilled off under diminished pressure. The remainder was a somewhat brownish, crystalline substance, which was purified by repeated crystallization from petroleum ether, the melting-point finally being  $112^{\circ}$ – $113^{\circ}$ . Analysis showed 27.73 per cent. bromine to be present; calculated 27.68 per cent. The yield was 25 grams of pure acetophenone-*p*-bromphenylhydrazone. A sample of the same body, prepared from acetophenone and *p*-bromphenylhydrazine proved its identity. The decomposition with hydrochloric acid is much slower and less satisfactory than it is in the case of acetone-*p*-bromphenylhydrazone.

If acetophenone-*p*-bromphenylhydrazone is slowly crystallized from alcohol, it separates in large cubes, resembling sodium chloride. It never shows a sharp melting-point for

the absolutely pure body begins to soften at  $106^{\circ}$ , and is only completely fluid at  $113^{\circ}$ . At a temperature somewhat above this it decomposes rapidly. Exposed to the air it is quickly oxidized, giving off a gas and changing to a black, tar-like substance. The fact that the body has not a sharp melting-point seemed to point to the existence of two isomers, but I have not, as yet, been able to prepare more than one acetophenone-*p*-bromphenylhydrazone.

*The Action of Bromine on the Phenylhydrazone of Pyruvic Acid.*

8.3 grams of the phenylhydrazone of pyruvic acid were suspended in ether and then 7.4 grams of bromine were added in the manner described above. The color of the bromine disappeared at once and the hydrazone went into solution. After the reaction was completed, the whole was extracted completely with 10 per cent. caustic potash, the alkaline extract acidified, the reddish precipitate dissolved in alcohol, and then separated by adding water. It was then a brown, amorphous powder. Its final purification is accomplished by dissolving it in potassium carbonate, boiling with animal charcoal, precipitating with dilute sulphuric acid, and finally recrystallizing from glacial acetic acid, when it appears as large yellow needles, melting at  $184^{\circ}$ . Analysis gave 31.1 per cent. bromine, calculated 31.4 per cent. The synthetical *p*-bromphenylhydrazone of pyruvic acid was identical with this body.

A chloroform solution of the phenylhydrazone of pyruvic acid ester is also easily brominated. The product melts at  $132^{\circ}$ , and is probably the *p*-brom compound.

*Bromination of Ethylidenepherylhydrazone.*

This reaction is essentially the same as that used in the formation of the acetone compound. The solid hydrobromide separates in ethereal solution, and the latter is shaken out with diluted caustic potash, the ether taking up all of the free body. After drying over fused sodium sulphate the solvent is evaporated *in vacuo* in the cold, by which means a crystalline product is obtained, separating from ligroin in yellow



plates melting at  $87^{\circ}$ . This body is, therefore, ethylidene-*p*-bromophenylhydrazone.<sup>1</sup> If the product is slightly warm, as is the case if the ester is distilled in a water-bath, oxidation sets in so readily on exposure to the air, that a violent explosion may result. This was the case with one of the preparations which I made.

The phenylhydrazone of methylethylketone is attacked by bromine in the same way, the hydrobromide separating at first in the form of a white, crystalline precipitate. The latter is quickly covered with a dilute solution of sodium carbonate, care being taken to exclude air by means of a current of carbon dioxide. The product then separates as an oil, the ethereal solution of which, if it is evaporated rapidly *in vacuo*, deposits crystals, which, however, melt as soon as the temperature of the room is reached. The *p*-brominated body is oxidized very rapidly on exposure to the air. If the ethereal solution is allowed to stand for an hour, after the addition of bromine and before the liberation of the base by means of the alkaline carbonate, then only *p*-bromophenylhydrazine is obtained, so that there can be no doubt that the *p*-brominated phenylhydrazone is in reality formed. Methylethylketone-*p*-bromophenylhydrazone is therefore separated into its component parts with extreme ease.

*Oxidation of Acetone-p-bromophenylhydrazone : p-Brombenzene-azo-i-propylene.*

10 grams of pure acetone-*p*-bromophenylhydrazone were covered with 50 cc. of ligroïn ( $56^{\circ}$ ), placed in an Erlenmeyer flask, well stoppered, and allowed to stand at winter temperatures. The stopper was removed from time to time and the flask shaken vigorously for two or three minutes, and then again placed aside. The reaction was completed as soon as all of the crystals had dissolved and the liquid had assumed a deep orange color. The ligroïn was then drawn off by a current of dry carbon dioxide and, as its volume became less, large, orange-colored prisms, with red dichroism, began to form. The latter were purified by redissolving in the same medium and evaporating as before. The melting-point is  $33^{\circ}$ , above

<sup>1</sup> Neufeld : Ann. Chem. (Liebig), 248, 95, gives the melting-point  $83^{\circ}$ .

which temperature the substance decomposes with explosive violence. When the prisms are exposed to the air, black spots soon begin to appear, and after a short time the entire substance breaks down with the evolution of nitrogen. Two grams of the body, ready for analysis and placed in a vacuum desiccator, exploded spontaneously with such violence that the apparatus was completely shattered and the fragments thrown to the corners of the room. The crystals cannot be kept for any great length of time, even in an atmosphere of carbon dioxide, although the decomposition under these circumstances is more gradual, and not violent. For this reason frequent recrystallizations are not possible. If the new body is gently warmed with concentrated sulphuric acid all the nitrogen is driven out. An analysis was therefore performed in the following manner: The substance was quickly weighed into a Kjeldahl flask, which had been previously filled with carbon dioxide; the apparatus was then connected with a Schiff azotometer, and a dropping-funnel containing concentrated, cooled sulphuric acid. After all air had been expelled the acid was rapidly added. Decomposition at once set in and was finally completed by gentle warming.

0.1880 gram substance gave 20.1 cc. nitrogen at  $14^{\circ}.5$ , and 737.8 mm.

	Calculated for $C_9H_9N_2Br$ .	Found.
N	12.3	12.4

A molecular weight determination was carried out as rapidly as possible, the solvent used being benzene.

Benzene,	30.8759		
I. Substance,	0.1452	I. Depression,	0.11
II. " "	0.5439	II. " "	0.4
Calculated, 225; Found, I. 226; II, 232.			

I was unable to obtain any accurate bromine determinations, as it was difficult to weigh and transfer the substance with sufficient rapidity; the numbers always appeared somewhat too low. The analyses of the perbromides, however, which are stable, were sufficiently accurate to make the analysis of the other compounds unnecessary.

The same body can be obtained in a much less pure condition by treating the hydrazone with yellow oxide of mercury in ethereal solution; the oxide is promptly reduced, and the liquid is at the same time colored red. After filtering and evaporating to dryness in a current of carbon dioxide, there remains an oil which gradually becomes semi-solid, and this has the properties of the body described above. It was found to be impossible successfully to recrystallize this product, as decomposition invariably set in before the desired object was accomplished. The change in acetone-*p*-bromphenylhydrazone is certainly due to oxygen, because a sample which was sealed in a small tube, from which the air had previously been expelled, suffered no alteration on standing for several months.

*p*-Brombenzeneazo-*i*-propylene is easily reduced to acetone-*p*-bromphenylhydrazone. 5 grams of the azo body were dissolved in absolute alcohol, sodium amalgam added, and one or two drops of hydrochloric acid, the contents of the flask being thoroughly shaken to hasten the change. The solution became colorless after a short time. When gas passed through freely, the supernatant liquid was decanted and diluted with water. Colorless, leafy crystals separated, which, when recrystallized from ligroïn, melted at 96°. This proved to be acetone-*p*-bromphenylhydrazone.

*The Action of Bromine on p-Brombenzeneazo-i-propylene.*

5 grams of the azo body were dissolved in cold chloroform, and then pure bromine gradually dropped in, the whole being kept cold. No change is observed during the first few seconds, but soon the bromine color disappears, and a yellow, crystalline body separates, there being no evolution of hydrobromic acid. The addition of bromine is continued until its color just becomes permanent. The precipitate is then filtered, dissolved in cold methyl alcohol, and the solution mixed with two or three times its own volume of ether; as a result yellow prisms gradually separate. The latter melt at 95°, with decomposition and separation of bromine. The same body can be prepared more readily by adding bromine to the

ligroin solution of *p*-brombenzeneazo-*i*-propylene, without taking the trouble previously to isolate the body. Bromine determinations gave the following results :

I. 0.0845 gram substance gave 0.1521 gram AgBr.

II. 0.0935 gram substance gave 0.1690 gram AgBr.

	Calculated for $C_9H_9N_2Br + 5Br$ .	I.	Found.	II.
Br	76.51	76.6		76.9

The perbromide is insoluble in ligroin. If it is warmed with water it gives off bromine. If boiled with benzene, bromine and a permanent gas separate. Repeated crystallization from luke-warm alcohol deprives the body of a portion of its bromine, giving a substance separating in yellow needles and melting at  $102^{\circ}$ – $105^{\circ}$ . This latter contains 73.63 per cent. bromine; calculated for  $C_9H_9N_2Br + 4Br$ , Br = 73.3 per cent. Continued boiling with alcohol finally causes complete decomposition of the perbromide.

It is possible to reduce the perbromide to acetone-*p*-bromphenylhydrazone. Two grams of substance melting at  $95^{\circ}$  were dissolved in alcohol, a drop or two of hydrochloric acid added, and then sodium amalgam poured in, the whole being vigorously shaken. As soon as the solution is colorless, it is poured off and diluted with water, when a crystalline body separates which is obtained from ligroin in flakes, melting at  $93^{\circ}$ – $94^{\circ}$ . This was consequently acetone-*p*-bromphenylhydrazone. Any doubt as to the nature of the products just described is finally removed by the following experiment: If acetone-*p*-bromphenylhydrazone (instead of the azo compound) is dissolved in chloroform, carefully cooled, and then bromine gradually added, hydrobromic acid is given off, and the same perbromide melting at  $94^{\circ}$ – $95^{\circ}$ , as was obtained from benzeneazo-*i*-propylene, and which in this latter instance is produced without the separation of hydrobromic acid, is separated on rubbing with a glass rod. Entirely different results are obtained, however, if the bromine is added carelessly, without the precaution being taken to cool thoroughly. The liquid then assumes a deep-violet color, nitrogen and hydrobromic acid separate rapidly, and the solution separates a certain

quantity of the hydrobromide of acetone-*p*-bromphenylhydrazone. If the latter is filtered and the mother-liquors (which now have the penetrating odor of halogen substitution-products of acetone) evaporated, there appear, in addition to a large quantity of tar, crystals which are free from nitrogen and melt at 87°. These have the appearance of *p*-dibrombenzene. In addition to the latter a small quantity of the hydrobromide of a body melting at 105° and probably *p*-bromphenylhydrazine, is obtained.

*Oxidation of Acetophenone-phenylhydrazone by Yellow Oxide of Mercury.*

10 grams of the hydrazone were dissolved in 25 cc. of ether, 1.5 gram-molecules of yellow oxide of mercury added, and the whole allowed to stand in a sealed tube, the latter being well shaken from time to time. The oxide is gradually reduced, the solution assumes a red color, and the reaction is complete after three to four days, no pressure being observed on opening the tube. The mercury and unchanged oxide are now filtered off, and the solution evaporated in a current of carbon dioxide. The remainder is a semi-solid mass which cannot be crystallized. It is rapidly oxidized when exposed to the air; heated on a platinum spatula it decomposes with a weak explosion; warmed with water or with sulphuric acid the substance gives off nitrogen; sodium amalgam reduces it, giving back acetophenonephenylhydrazone. There seems scarcely any doubt that this body is benzene-azo-*i*-styrene, but as yet it has not been obtained in a pure state. Better results are obtained with the *p*-brominated compound. If a sealed tube, filled as above, is allowed to stand too long, say for two or three weeks, there is then considerable pressure on opening, and none of the decomposable oil is obtained, obviously because the azo body has been completely broken down.

*Oxidation of Acetophenone-*p*-bromphenylhydrazone : *p*-Brombenzene-azo-*i*-styrene.*

10 grams of acetophenone-*p*-bromphenylhydrazone were covered with 50 cc. petroleum ether, the flask stoppered and



exposed to the temperature of winter. Care was taken to admit the air from time to time, just as was the case with the corresponding acetone derivative. Oxidation took place more slowly in this case but, after ten days, all had gone into solution, and at the same time the liquid had assumed a deep-red color. The petroleum ether was now cooled to  $-20^{\circ}$ , and a separation of canary-colored prisms took place. The latter were filtered, once more dissolved, and again crystallized. They melted at  $48^{\circ}$ , and decomposed violently above that temperature. Exposed to the air they behaved as did benzeneazo-*i*-propylene, exploding after a certain time. The bromine was determined by the lime method, in a long tube, care being taken to weigh as quickly as possible.

0.1340 gram substance gave 0.0851 gram AgBr.

	Calculated for $C_{14}H_{11}N_2Br$ .	Found.
Br	27.8	27.00

The substance decomposes, when gently warmed with sulphuric acid, nitrogen being evolved.

2 grams of the azo body were dissolved in alcohol, a drop or two of hydrochloric acid added, and then sodium amalgam poured in. As soon as the color of the solution disappeared, the supernatant liquid was poured off and diluted with water. The crystalline precipitate separated from alcohol as a body melting at  $104^{\circ}$ , and having all of the properties of acetophenone-*p*-bromophenylhydrazine.

If *p*-bromobenzeneazo-*i*-styrene is dissolved in chloroform, well cooled, and bromine gradually added, a precipitate at once begins to appear, without evolution of hydrobromic acid. This substance crystallizes from alcohol, after ether has been added, in long prisms melting at  $108^{\circ}$ . In appearance and properties these are very closely like those obtained from the corresponding acetone derivative. The estimations of bromine gave results lying between the numbers required for  $C_{14}H_{11}N_2Br + 7Br$  and those for  $C_{14}H_{11}N_2Br + 6Br$ . Found, bromine I. 74.1 per cent., II. 74.5 per cent. Calculated for  $C_{14}H_{11}N_2Br + 7Br$ ;  $Br = 75.5$ ; for  $C_{14}H_{11}N_2Br + 6Br$ ,  $Br = 73.03$ . From these results it follows that this perbromide is a

mixture of the two bodies. Owing to its close resemblance to the perbromide of the corresponding acetone derivative, no further work was done with it at present.

It was not found possible to oxidize acetophenone-*p*-bromophenylhydrazone to an azo body by means of yellow oxide of mercury. The action takes place so slowly in the cold that the resulting compound is further decomposed. If the solution is warmed, the oxide is reduced rapidly, but on the other hand the azo body is at once completely broken down with the evolution of nitrogen.

In order to remove any doubt as to the nature of the bodies which have been described above, I have studied the behavior of benzoylphenylhydrazine. The work of Freer and Sherman<sup>1</sup> on formylphenylhydrazine has demonstrated that, in all probability, the acylphenylhydrazines have the structure  $\text{RO.NH.NH.C}_6\text{H}_5$ , so that they in reality constitute a series of hydrazo compounds.

*The Action of Bromine on Benzoylphenylhydrazine: Benzoyl-*p*-bromophenylhydrazine.*

Monobenzoylphenylhydrazine (20 grams) was suspended in 250 cc. of absolute ether, cooled in a freezing-mixture, and then 2 gram-molecules of bromine gradually added, the whole being well stirred. The bromine color disappeared at once, and a violent evolution of hydrobromic acid took place. After the action was complete, the resulting compound was filtered, washed with ether, and then quickly covered with dilute potassium hydroxide solution, by which means a white, crystalline body formed. The latter separated from alcohol in shiny, white leaflets, melting at  $156^\circ$ , with decomposition. The alcoholic mother-liquors, when diluted with water, deposit a smaller quantity of another body which fuses at  $125^\circ$ . This is probably the *m*-compound. It has not, as yet, been further investigated. Boiling hydrochloric acid splits the substance of melting-point  $156^\circ$  into benzoic acid and *p*-bromophenylhydrazine.

The first bromination of benzoylphenylhydrazine never is quite complete, for a certain quantity of unchanged body al-

<sup>1</sup> This JOURNAL, 18, 570.



ways remains. It is, therefore, advisable to carry out a bromine determination with the crude product, and then to repeat the above operation, using the calculated quantity of bromine. After subsequent recrystallization, the pure benzoyl-*p*-bromphenylhydrazine, melting at 156°, is obtained. Analysis resulted as follows :

0.4955 gram substance gave 0.2189 gram AgBr.

	Calculated for $C_{13}H_{11}N_2OBr$ .	Found.
Br	27.41	27.42

*Oxidation of Benzoyl-p-bromphenylhydrazine. p-Brombenzene-azobenzoyl.*

Fischer<sup>1</sup> has already studied the oxidation of benzoylphenylhydrazine, but he obtained only a dark red oil, which he was able to reduce back to benzoylphenylhydrazine. The oil decomposed violently on heating and was completely broken down by boiling water. It undoubtedly, therefore, contained an azo body. Better results are obtained with the *p*-brom-compound.

10 grams of benzoyl-*p*-bromphenylhydrazine were suspended in 100 cc. absolute ether, 1.5 gram-molecules of yellow mercuric oxide added, and the whole set aside, the flask being well shaken from time to time. Reduction of the oxide takes place slowly, but after twelve hours the benzoyl-*p*-bromphenylhydrazine had dissolved and the liquid had assumed a red color. The solution was now filtered and the ether evaporated *in vacuo*, a red, crystalline body separating. This residue was extracted with cold ligroin, by which means the azo body was dissolved, and unchanged substance left behind. *p*-Brombenzeneazobenzoyl separated in red, leaf-like plates, when this solvent was evaporated in the cold. This operation was repeated several times, the body being finally dissolved in alcohol and recrystallized by adding water. Large red plates, melting at 69° and giving the following results on analysis, were obtained :

0.1877 gram substance gave 0.3696 gram CO<sub>2</sub>, and 0.0533 gram H<sub>2</sub>O.

<sup>1</sup> Ann. Chem. (Liebig), 190, 126.

	Calculated for $C_{13}H_9N_2OBr$ .	Found.
C	53.98	53.70
H	3.11	3.15

When pure, the azo body is perfectly stable in the air, heated in a tube it begins to give off nitrogen at  $133^\circ$ , and forms benzoic acid at  $142^\circ$ .

The reduction is easily accomplished. Two grams were dissolved in alcohol, sodium amalgam added, and the whole well shaken. As soon as the solution became colorless, it was decanted and acidified. The resulting precipitate, when recrystallized from alcohol, melted at  $155^\circ$ , and proved to be benzoyl-*p*-bromophenylhydrazine.

*The Action of Bromine on p-Brombenzeneazobenzoyl.*

The red crystals of the azo body were dissolved in chloroform and gradually mixed with a slight excess of bromine. Reaction set in, and only traces of hydrobromic acid were given off. At the same time a dark-red oil separated. This latter solidified completely on standing at a low temperature. The chloroform was then poured off and the crystals were spread on a porous plate. Two bodies were present, garnet-red prisms, melting at  $123^\circ$  with decomposition, and yellow needles, fusing at  $106^\circ$ . The red crystals rapidly lose bromine in the air and change to the yellow body. They were separated mechanically as soon as possible, and analyzed without further purification. Found, bromine 68.7 per cent.; calculated for  $C_{11}H_9N_2OBr + 5Br$ , Br = 69.6 per cent.<sup>1</sup>

If the red substance is covered with alcohol it at once changes to the yellow one. If the bromination is carried on as above, glacial acetic acid being substituted for chloroform, then the yellow body melting at  $106^\circ$  is alone produced. Analysis of the latter gave 65.7 per cent. bromine; calculated for  $C_{11}H_9N_2OBr + 4Br$ , Br = 65.7 per cent.

If either perbromide is boiled with alcohol, the latter is oxidized to aldehyde, nitrogen separates, and the solution be-

<sup>1</sup> These figures agree very nearly with those calculated for the perbromide of diazobenzene (calculated 69.56 per cent.), and it is possible that in some instances this body is formed. This question has not as yet been decided, but the whole subject of these perbromides and their decomposition will be thoroughly investigated next year.

comes colorless. When cooled, two bodies which are difficult to separate by fractional crystallization, appear; the one is in long needles, melting at  $119^{\circ}$ – $120^{\circ}$ , the other in prisms fusing at  $87^{\circ}$ . Neither contains nitrogen. Judging from the analysis and molecular weight, these bodies are bromine substitution-products of phenols, but as it has been demonstrated that this decomposition of perbromides of the class under study is a general one, and as it perhaps will lead to new methods of formation of bromine substitution-products of benzene no further work was done along this line.

*The Action of Bromine on Monoacetylphenylhydrazine: Acetyl-*p*-bromphenylhydrazine.*

This reaction was carried out exactly as with the corresponding benzoyl derivative. The resulting body at first is fluid, but solidifies after a time, especially if it is spread on a porous plate. Crystallized from alcohol with the addition of animal charcoal, it melted at  $161^{\circ}$ ; the yield was unsatisfactory. When treated with mercuric oxide the body is changed to a red oil, which gives a yellow perbromide on treatment with bromine; this perbromide, when it is boiled with alcohol, decomposes in the same way as those described above.

The close resemblance between *p*-brombenzeneazobenzoyl, *p*-brombenzeneazo-*i*-propylene, and *p*-brombenzeneazo-*i*-styrene seems to remove all doubt as to the character of the latter two compounds.

In view of the above work it seemed desirable to discover whether acetone-*p*-bromphenylhydrazone, which is so easily oxidized to an azo body, would also take up hydrocyanic acid in the same way as the phenylhydrazones of Miller and Plöchl.<sup>1</sup> No action takes place if the hydrazone is diluted with absolute ether, but if it is covered with pure hydrocyanic acid and sealed in a tube, a gradual change takes place, the leaf-like crystals being converted into prisms. The reaction is completed in three weeks. The tube is then opened, the excess of hydrocyanic acid evaporated, and the product recrystallized from ligroin. It forms hard prisms which differ markedly from the original substance by being perfectly stable

<sup>1</sup> Ber. d. chem. Ges., 25, 2058.

in the air; the melting-point is  $95^{\circ}$ – $96^{\circ}$ . A nitrogen determination gave the following results:

0.1116 gram substance gave 16.8 cc. nitrogen at  $19^{\circ}$  and 736 mm.

	Calculated for $C_{10}H_{13}N_3$ .	Found.
N	16.5	16.8

This result proves that acetone-*p*-bromphenylhydrazone takes up hydrocyanic acid and if, as seems most probable from the above work, this body is in reality *p*-brombenzene-

hydrazo-*i*-propylene,  $\begin{array}{c} CH_2 \\ || \\ C-NH.NH.C_6H_4.Br \\ | \\ CH_3 \end{array}$ , the addition must

take place to the unsaturated pair of carbon atoms, the same must then be true of the other easily oxidized ketonephenylhydrazones which Miller and Plöchl investigated. From the researches of the latter it appears that the phenylhydrazone of pyruvic acid, which undoubtedly has the true hydrazone structure, does not take up hydrocyanic acid, but, on the other hand, acetophenone-phenylhydrazone, which can also be easily oxidized, is incapable of taking up hydrocyanic acid, so that, in the present state of our knowledge, we must conclude that this reaction can neither prove nor disprove the hydrazo structure.

#### *Reactions with the Phenylhydrazone of Pyruvic Acid.*

The phenylhydrazone of pyruvic acid is a body which shows an entirely different behavior from those which have been cited above, with the sole exception that it can be converted into the *p*-brom compound with equal ease. The substance is remarkably stable, does not oxidize in the least when exposed to the air, and is not changed to an azo body by mercuric oxide, neither does it form a tetrazone, as Von Pechmann found to be the case with benzalphenylhydrazone.

#### *The Action of Mercuric Oxide on the Phenylhydrazone of Pyruvic Acid.*

If the phenylhydrazone of pyruvic acid (15 grams), yel-

<sup>1</sup> Ber. d. chem. Ges., 26, 1045.

low oxide of mercury (25 grams), and alcohol (100 cc.) are boiled in a vessel provided with an inverted condenser, the oxide is gradually reduced, and exactly one-half of the possible quantity of carbon dioxide separates (calculated  $\text{CO}_2$ , 12.6 per cent.; found, 12.9 per cent.); the evolution of gas then ceases and the reaction is complete. The mercury compound is then filtered off, and the alcohol evaporated *in vacuo* until crystals begin to appear. On standing, a yellow, crystalline powder separates. This is filtered off, extracted with 10 per cent. caustic potash in order to remove any possible unchanged substance, and at last recrystallized from alcohol with the addition of animal charcoal. The compound forms yellow needles, scarcely soluble in cold alcohol, easily taken up by the hot alcohol, separating from dilute acetic acid in large crystals melting at  $186^\circ.5$ .

0.1102 gram substance gave 0.0619 gram  $\text{H}_2\text{O}$ , and 0.2642 gram  $\text{CO}_2$ .

0.1522 gram substance gave 25.2 cc. nitrogen at  $18^\circ$  and 742.3 mm.

	Calculated for $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2$ .	Found.
C	65.8	65.38
H	5.8	6.24
N	18.0	18.66

The molecular weight determination was made in a solution of glacial acetic acid.

Solvent, 22.08

Depression, 0.18

Substance, 0.3065

Calculated 310; found 308.

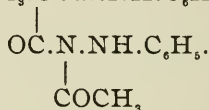
This body is therefore formed from the hydrazone of pyruvic acid according to the following equation:



Reduction in acetic acid solution by means of zinc dust gave only aniline and tarry products. On adding alkali a large quantity of phenylisonitril was produced. Hydrochloric acid (33 per cent.) at  $100^\circ$ , chars the substance, splitting off one-half of the phenylhydrazine. No other body could be isolated.



Three grams of the substance were boiled with 2 gram-molecules of alcoholic potash for half an hour. On evaporating the alcohol and acidifying, a yellow body separated. This was filtered and recrystallized from acetic acid. It proved to be the phenylhydrazone of pyruvic acid. The mother-liquors were extracted with ether, the solvent evaporated, and the remainder recrystallized from benzene, when needles, melting at  $126^{\circ}$ , separated. Comparison showed these to be monoacetylphenylhydrazine. This oxidation product is therefore split into acetylphenylhydrazine and the phenylhydrazone of pyruvic acid by means of alkalis. It is therefore most probably the acetylphenylhydrazide of the phenylhydrazone of pyruvic acid,  $\text{CH}_3\text{C} : \text{N.NH.C}_6\text{H}_5$ ,



The action of mercuric oxide on the hydrazone of pyruvic acid is therefore radically different from its action on the phenylhydrazones described above; the hydrogen present in the phenylhydrazine group is not attacked at all, but instead of this, carbon dioxide is eliminated, 2 molecules are joined, and the ethylidene group in one portion is oxidized to acetyl. This change would seem to prove that the phenylhydrazone of pyruvic acid has a constitution different from that of the class of bodies which can be oxidized to substances having the azo structure. It therefore is a true hydrazone, the others being hydrazo compounds. Other true hydrazones, such as benzaldehydrazone, as Von Pechmann demonstrated,<sup>1</sup> also behave differently from hydrazo compounds, for amyl nitrite or mercuric oxide changed this body into dibenzaldiphenyltetrazone. Many phenylhydrazones are not attacked at all by mercuric oxide. This is the case with the phenylhydrazone of pyruvic acid ester.

In view of the above results, it was necessary, if possible, to discover some case in which both classes of bodies are formed from one and the same ketone or aldehyde, as was mentioned in the introduction, all such attempts have as yet

<sup>1</sup> Ber. d. chem. Ges., 26, 1045.

failed with acetone-*p*-bromphenylhydrazone and with acetophenone-*p*-bromphenylhydrazone. On the other hand, the desired substances seem to exist in the case of the benzoïnphenylhydrazones.

*Reactions with the Phenylhydrazones of Benzoïn.*

Smith and Ransom<sup>1</sup> have already demonstrated that an isomer of ordinary (159°) benzoïnphenylhydrazone can be obtained under certain circumstances. This isomer melts at 106° and, according to the usually accepted views, two bodies were considered to be stereoisomeric. That this is not the case, however, and that they are structurally different, is demonstrated by the facts stated below.

*The Action of Benzoyl Chloride on  $\beta$ -Benzoïnphenylhydrazone:  
 $\gamma$ -Benzoïnphenylhydrazone.*

Pure  $\beta$ -benzoïnphenylhydrazone, melting at 106°, is prepared by boiling a mixture of 20 grams of pure benzoïn and 10 grams of recrystallized phenylhydrazone in alcoholic solution in a vessel provided with an inverted condenser for three and a half hours. On cooling and standing in an ice chest over night, crystals separate which are filtered and purified from alcohol. On adding water to the mother-liquors, a mixture of the  $\alpha$ - and  $\beta$ -compounds is obtained. Pure  $\beta$ -benzoïnphenylhydrazone must be perfectly soluble in cold glacial acetic acid.

5 grams of this body were dissolved in absolute ether and then an equal amount of pure benzoyl chloride added. After a few hours the solution became turbid and in the course of two days the reaction was completed. A mixture of shiny leaflets and an amorphous powder had now separated and the ether was colored red. The precipitate was repeatedly triturated with water, by which means the soluble, amorphous substance, which is the hydrochloride of a base, is separated, and the residue is finally recrystallized from alcohol. The pure substance weighed 2.7 grams. It forms plates with mother-of-pearl luster, melting at 162°.

I. 0.1879 gram substance gave 0.5452 gram CO<sub>2</sub>, and 0.1040 gram H<sub>2</sub>O.

<sup>1</sup> This JOURNAL, 16, 103.



II. 0.1667 gram substance gave 14 cc. nitrogen at  $31^{\circ}$  and 743 mm.

	Calculated for $C_{20}H_{18}N_2O$ .	I.	Found.	III.
C	79.43	79.13		....
H	5.96	6.09		....
N	9.27	....		9.42

The molecular weight determinations were carried out in a solution of methyl oxalate.

Methyl oxalate I.	27.483	Depression I.	0.08
" " II.	33.313	" II.	0.19
Substance I.	0.1281		
" II.	0.4168		

Calculated 302 ; Found, I. 298 ; II. 339.

These result show that this body is a third benzoïnphenylhydrazone. In appearance and solubility it differs entirely from the other two; the latter crystallize from alcohol in needles and are soluble in ether, the former separates from the same medium in plates, and is nearly insoluble in ether. I will designate this new compound as  $\gamma$ -benzoïnphenylhydrazone during the further discussion.

When the ethereal mother-liquors, obtained during the preparation of  $\gamma$ -benzoïnphenylhydrazone were evaporated, there remained a dark-red oil which had a strong odor of benzoyl chloride. On standing, a small quantity of the new body, and finally long, needle-like crystals separated from this. The benzoyl chloride was removed from the latter as far as possible, by adding petroleum ether and then pumping off the solution rapidly. On evaporation, 2.8 grams of unchanged benzoyl chloride remained. This separation is not strictly accurate, as a certain proportion of the chloride is always retained by the tarry mass surrounding the crystals, so that it must be assumed that the major portion remained unchanged during the reaction. A part is undoubtedly used up in forming the soluble hydrochloride above referred to, and some enters into the formation of the sticky decomposition-product. Further experiments with much less than the calculated quantity of benzoyl chloride demonstrated that such a large addition of that substance is by no means necessary to bring

about the change, so that benzoyl chloride does not directly enter into the composition of the bodies which are produced. The long, needle-like crystals were covered with a thick tar which was insoluble in petroleum ether. They were therefore spread on a porous plate and finally repeatedly recrystallized from alcohol, their total weight finally being 1.7 grams. This body contained no nitrogen, melted at  $94^{\circ}$ – $95^{\circ}$ , and comparison with other samples proved it to be benzil. The formation of this latter body is not due to absorption of oxygen from the air, for the same result is obtained if the reaction is allowed to go on in a flask filled with carbon dioxide. The total result was therefore as follows: From 5 grams of  $\beta$ -benzoïnphenylhydrazone and 5 grams of benzoyl chloride I obtained 2.7 grams of  $\gamma$ -phenylhydrazone, 1.7 grams of benzil, 3 grams of unchanged benzoyl chloride, and the remaining 2.6 grams consisted of the non-crystallizable tar and the small proportion of soluble hydrochloride. Benzoyl chloride therefore reacts with  $\beta$ -benzoïnphenylhydrazone in a most unexpected manner. The greater part is changed into the  $\gamma$ -phenylhydrazone, which undergoes no further change, and another portion forms benzil, and as a result of this secondary change, probably also the tarry products above referred to.<sup>1</sup> The origin of the benzil is not at all plain; it does not seem probable that it is produced by the oxidation and subsequent splitting down of the benzoïnphenylhydrazone, neither does it seem likely that it results from a union of two benzoyl groups derived from the chloride. A further detailed investigation of this point with larger quantities of material, is necessary.

Neither  $\alpha$ - nor  $\gamma$ -benzoïnphenylhydrazone reacts with benzoyl chloride at ordinary temperatures.

There are some further points in connection with the preparation of  $\alpha$ - and  $\beta$ -benzoïnphenylhydrazones which should be mentioned. Pickel<sup>2</sup> and Vogeltheer<sup>3</sup> obtained the  $\alpha$ -compound only, their method consisting in boiling an alcoholic

<sup>1</sup> Smith and Ransom found that  $\beta$ -benzoïnphenylhydrazone was completely decomposed by acetyl chloride. The formation of tarry products is always observed when benzoyl chloride acts on the hydrazones.

<sup>2</sup> Ann. Chem. (Liebig), **232**, 229.

<sup>3</sup> Ber. d. chem. Ges., **25**, 637.

solution of benzoïn and phenylhydrazine for some time, then evaporating and extracting the syrup which remained with acetic acid, in order to remove phenylhydrazine. The reason why they obtained no  $\beta$ -phenylhydrazone was not because it was not formed, but because this substance is soluble in acetic acid, and was therefore removed with the excess of phenylhydrazine. According to Smith and Ransom, nearly pure  $\beta$ -phenylhydrazone is obtained by fusion of the calculated quantities of benzoïn and phenylhydrazine over a free flame. It is true that under these circumstances a certain amount of the pure  $\beta$ -body can be obtained from the first products of recrystallization, but the greater proportion consists of a mixture of the  $\alpha$ - and  $\beta$ -varieties, melting at  $103^{\circ}$ – $105^{\circ}$ .<sup>1</sup> Such a substance, crystallizing in needles and fusing at  $103^{\circ}$ – $105^{\circ}$  can be obtained by bringing together the phenylhydrazones melting at  $106^{\circ}$  and  $159^{\circ}$ . In addition to the hydrazones, the product of direct fusion also contains a certain amount of unchanged benzoïn. The latter must be removed by treatment with cold ether, which leaves this body behind. If the substance is purified in this way and then recrystallized from alcohol, extraction of the crystals with acetic acid will take out the  $\beta$ -phenylhydrazone. The residue then, without recrystallization, melts at  $156^{\circ}$ – $157^{\circ}$  and consists of the  $\alpha$ -variety. The same results are obtained by boiling an alcoholic solution of pure benzoïn with pure phenylhydrazine in a vessel connected with an inverted condenser for three and one-half hours. If the solution, which has then assumed a slightly yellow color, is allowed to stand, pure  $\beta$ -phenylhydrazone, completely soluble in acetic acid, at first separates. If the latter is filtered, and the mother-liquors diluted with water, the resulting crystalline precipitate melts at  $103^{\circ}$ – $105^{\circ}$ . This is a mixture of the  $\alpha$ - and  $\beta$ -varieties. Extraction with glacial acetic acid and recrystallization of the insoluble remainder then leads to the pure  $\alpha$ -hydrazone. This is, to the best of my knowledge, the best way to prepare  $\alpha$ -benzoïn-phenylhydrazone.

On page 115 of their article, Smith and Ransom state that  $\beta$ -benzoïnphenylhydrazone is converted into the  $\alpha$ -body by

<sup>1</sup> The proportion of  $\beta$  to  $\alpha$  is about 6 to 1.

boiling in alcoholic solution with two gram-molecules of phenylhydrazine, a 50 per cent. yield being obtained. On carefully repeating this experiment with pure  $\beta$ -benzoïnphenylhydrazone, I found that from 2 grams I could obtain only 0.05 gram of the  $\alpha$ -modification, so that only a minimal quantity of the latter body is formed. Smith and Ransom's result, therefore, was due to the fact that they, in reality, were dealing with a mixture.

*The Oxidation of  $\beta$ -Benzoïnphenylhydrazone.*

It is impossible successfully to oxidize this substance by means of mercuric oxide in the cold, because the change takes place very slowly, if at all. Better results are obtained by passing nitrogen trioxide gas into the ethereal solution. This method has been used by Dr. Gomberg, of this laboratory, in converting benzenehydrazotriphenylmethane into benzeneazotriphenylmethane.

5 grams of pure  $\beta$ -benzoïnphenylhydrazone were dissolved in 100 cc. absolute ether, well cooled by means of a freezing-mixture, and nitrogen trioxide was then slowly passed in. The solution at once began to turn red, and the reaction is completed as soon as a somewhat greenish color becomes visible. The whole was then immediately extracted repeatedly with a dilute cold solution of potassium carbonate, by which means the ethereal solution finally changed to a thick mass of red, flaky needles. The operation was continued until the carbonate just began to assume a permanent reddish tint, a sign that the excess of trioxide had been removed. The supernatant ether, which contained the new body, was then separated and filtered. On drying the mother-liquors and evaporating *in vacuo*, a further quantity of the new body, in addition to benzoic aldehyde, could be obtained. In all there were formed 3.3 grams of the red crystals, 0.35 gram of benzoic aldehyde (determined as benzalphenylhydrazone, and representing 1.00 gram of the original body) and 0.7 gram of a non-crystallizable tar.

The substance formed by this reaction crystallizes from alcohol in large, red needles, melting at  $137^{\circ}$  with decompo-

sition and evolution of the red vapors of nitrogen trioxide. Treated with bromine, in chloroform solution, the body gives a fine, deep-yellow perbromide.

I. 0.1751 gram substance gave 0.3519 gram  $\text{CO}_2$  and 0.0620 gram  $\text{H}_2\text{O}$ .

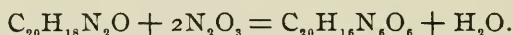
II. 0.2002 gram substance gave 0.3978 gram  $\text{CO}_2$  and 0.682 gram  $\text{H}_2\text{O}$ .

III. 0.2101 gram substance gave 0.4196 gram  $\text{CO}_2$  and 0.077 gram  $\text{H}_2\text{O}$ .

IV. 0.1551 gram substance gave 27 cc. nitrogen at  $25^\circ$  and 735 mm.

	Calculated for $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_6$ .	I.	II.	Found. III.	IV.
C	55.05	54.25	54.19	54.48	....
H	3.89	3.93	3.77	4.17	....
N	19.24	....	....	....	18.7

Another analysis of a product recrystallized from acetic ether, entirely in the cold, gave 55 per cent. carbon and 4.34 per cent. hydrogen. The analytical data were unfortunately lost. These numbers agree best with a body formed according to the following equation :



If a direct addition of two molecules of nitrogen trioxide to one of the azo body had taken place, the product would have the formula,  $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_7$ , which requires 52.86 per cent. carbon and 3.82 per cent. hydrogen. It is possible that a certain percentage of nitrogen trioxide is always separated on recrystallization, thereby increasing the numbers for carbon and hydrogen, but in view of the close concordance of results obtained from several recrystallizations, this does not seem likely.

A molecular weight determination was made, methyl oxalate being used as the solvent :

Methyl oxalate, 26,973.      Depression,  $0.135^\circ$ .  
Substance, 0.2198.

Calculated, 443 ; found, 320.

It is evident from this result that a certain amount of dissociation has taken place, a portion of the nitrogen trioxide having separated. This view is confirmed by the fact that if the solution is allowed to stand and the depression is deter-



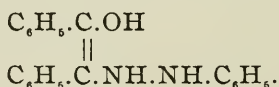
mined from time to time, the latter constantly increases until the molecular weight 170 is reached, the calculated molecular weight, if complete separation into three molecules had taken place, would be 141. As to the constitution of this body, nothing definite can be said; most probably it is formed by addition of the oxide of nitrogen to the azo body, much in the same way as the perbromides are produced; that the original nitrogen atoms now possess the structure of an azo body is rendered extremely probable by the fact that this new substance takes up bromine to form a perbromide. The red needles dissolve in caustic potash with an intense purple color. If the solution is instantly acidified, the original body again separates; if it is allowed to stand, complete decomposition, with the formation of tarry products, sets in. Sodium carbonate, in aqueous solution, has little effect. If alcohol is added, the same purple color appears. Boiling with phenylhydrazine in alcoholic solution seems to cause no change. When the body is dissolved in alcohol and reduced by means of sodium amalgam, large quantities of ammonia are formed, and the solution soon becomes colorless; water then throws down an amorphous, white body which, however, is extremely unstable, rapidly taking up oxygen from the air and forming a deep-red, non-crystallizable oil. If the solution is acidified and extracted with ether, and the latter evaporated, a tarry mass remains. As yet I have not succeeded in converting the red substance either into the corresponding azo body or into  $\beta$ -benzoïnphenylhydrazone. The solutions in methyl oxalate and in benzene are yellow, and not red, as would be expected. The constitution of this substance will be the subject of further investigation.

If the new body is dissolved in chloroform, and bromine, in excess, added, the latter is instantly taken up, without the evolution of hydrobromic acid. On evaporating the solvent, the entire residue changes to a mass of yellow crystals, which melt, after recrystallization from acetic ester, at  $161^{\circ}$ – $162^{\circ}$  with decomposition.

A bromine determination gave 34.7 per cent. bromine; calculated for  $C_{20}H_{16}N_2O_6 + 3Br$  is 35.4. Carbon and hy-

drogen came somewhat too high for this formula, so that probably a portion of the oxide of nitrogen was driven off by the action of bromine, and this is rendered more probable by the fact that the analytical results vary with each recrystallization, so that it has as yet not been possible to obtain this substance in a state of purity. The figures demonstrate beyond a doubt, however, that the nitrogen trioxide is not to any extent expelled by the bromine, the latter simply adding itself. The appearance and properties of this perbromide are so closely like those of the others which have been described, that there seems little doubt as to the azo structure of the body which is the basis of the formation. The great stability of the addition-product is rather peculiar, but then the perbromides are equally stable. A further proof that the above view is correct is found in the fact that Gomberg, in oxidizing his benzenehydrazotriphenylmethane to benzeneazotriphenylmethane by the same method, obtained a product which on analysis always gave too high numbers for the nitrogen. This result is in all probability due to the formation of a certain proportion of a similar addition-product.

Similar results are obtained on treating ethyridenephnylhydrazone with nitrogen trioxide, and the resulting body, also, only retains a portion of the oxide. There seems to be no doubt, considering the above facts, that  $\beta$ -benzoïnphenylhydrazone has the structure represented by the formula,



The action of nitrogen trioxide on  $\alpha$ -benzoïnphenylhydrazone takes place in an entirely different manner. One gram of the body was dissolved in absolute ether, cooled with a freezing-mixture, and nitrogen trioxide gas slowly run in. A white, crystalline precipitate instantly appeared, so that the liquid was soon changed to a thick paste. If the action is continued for too great a length of time, the quantity of this new body diminishes and the solution assumes a red color. This white substance is rapidly decomposed on exposure to the air. In order to isolate it, it was therefore filtered in a

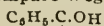


Brühl apparatus in a current of carbon dioxide, washed with ether and, as soon as dry, treated with a cold solution of sodium carbonate. The latter reagent changes the body to a white, crystalline powder which separates from alcohol in needles, melting at  $212^{\circ}$  to  $213^{\circ}$ . The quantity at my disposal has heretofore been insufficient for the purposes of analysis. It is most probably the tetrazone, the original precipitate being the nitrite of that body. I was unable to obtain any of the red body derived from the  $\beta$ -hydrazone, on using the pure  $\alpha$ -body, but I did observe its formation when using a sample prepared according to Smith and Ransom's directions. This result is probably due to the fact that some of the  $\beta$ -variety was present in the latter instance.  $\gamma$ -Benzoïn-phenylhydrazine apparently does not react with nitrogen trioxide.

As a result of this investigation we must therefore accept the existence of three benzoïnphenylhydrazones, the low-melting individual exhibiting different chemical characteristics from the others, and, as was remarked above, it is probably the hydrazo-compound. The  $\alpha$ - and  $\gamma$ -phenylhydrazones differ but little in their melting-points ( $3^{\circ}$ ), but do not resemble each other, either in appearance or solubility. This small distinction in the melting-points is entirely different from what would be expected if they were stereoisomers, such as the bodies described by Hantzsch and Krafft<sup>1</sup> and Hantzsch and Overton<sup>2</sup>, for these substances all show a difference of  $30^{\circ}$ – $50^{\circ}$ . According to our present views, it is difficult to see what other distinction, excepting that of geometric isomerism, there can be between the two classes of phenylhydrazones described by Hantzsch, but the same also applies to  $\alpha$ - and  $\gamma$ -benzoïnphenylhydrazones.<sup>3</sup> The interval between the melting-points of  $\beta$ - and  $\alpha$ -benzoïnphenylhydrazones is  $53^{\circ}$ , and therefore almost the same as that in the case of the

<sup>1</sup> Ber. d. chem. Ges., **24**, 3525.

<sup>2</sup> *Ibid.*, **26**, 9; compare Wegschneider, Monatshefte f. Chem., **17**, 245.



<sup>3</sup> The structure  $\text{C}_6\text{H}_5\text{C}(\text{NH.N.C}_6\text{H}_5)$  is also possible for  $\gamma$ -phenylhydrazone, but



it is hardly probable.

bodies of Hantzsch, yet the substances certainly are distinct in their chemical behavior. In view of these considerations it is, therefore, desirable that this entire relationship should be subjected to further investigation.

Experiments with Fischer's two ethylenephénylhydrazones<sup>1</sup> were also undertaken, but as in this case a body was formed which probably is a representative of a new class of substances, the nitrosophénylhydrazones, a detailed investigation was left for the future. A few results which have an immediate bearing on the present work, will, however, be detailed here.

Two grams of the  $\beta$ -phénylhydrazone, melting at  $60^\circ$ , were dissolved in ether, cooled in a freezing-mixture, and then nitrogen trioxide slowly added. A white precipitate appeared at once and the reaction was complete as soon as the solution had assumed a greenish tint. The resulting substance was then filtered off, and the ether repeatedly extracted with small quantities of dilute caustic potash until the latter retained its alkalinity. It was then dried over fused sodium sulphate and evaporated *in vacuo*, a yellow crystalline body remaining, which was purified by dissolving in alcohol and precipitating with water, when it was found to melt at  $83^\circ$ . The crystals behave very much like those of the red body derived from  $\beta$ -benzoïnphénylhydrazone; they decompose when heated, and give off nitrogen trioxide, not, however, in such quantity as does that substance. Bromine yields a characteristic perbromide, which decomposes when it is boiled with alcohol in the same way as do the others described above. The white precipitate, which at first separated, was filtered off, washed with ether and dried in a vacuum desiccator. When heated it explodes with the greatest violence; 0.05 gram, carefully heated in a test-tube, decomposed with a loud report and shattered the glass into powder. If this body is kept in a vacuum for any length of time, it gradually breaks down, turning red, and to a great extent loses its explosive property; the change is complete at the end of a week. This substance is probably the nitrosophénylhydra-

<sup>1</sup> Ber. d. chem. Ges., 29, 793.

zone, and, as it had no direct bearing on the present work, it was reserved for future study.

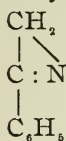
$\beta$ -Ethylidenephénylhydrazone (m. p.  $60^{\circ}$ ) is readily oxidized by yellow oxide of mercury. If the substance is dissolved in ether, the reaction at once sets in at ordinary temperatures, and is complete in twelve hours. After filtering and evaporating *in vacuo*, a red oil is left, which contains a certain quantity of yellow crystals. The latter, when purified by means of ligroïn, melts at  $80^{\circ}$ , and their analysis and molecular weights proved them to be ethylidenephénylhydrazone. These crystals are not attacked by oxide of mercury in the cold, and they consist of the modification which Fischer supposed might be a mixture of the  $\alpha$ - and  $\beta$ -bodies,<sup>1</sup> but which that investigator also considered as a possible third isomer. According to the above result they certainly could contain no  $\beta$ -body, for they were twice treated with an excess of mercuric oxide, so that Fischer's second supposition becomes more probable. This is further borne out by the fact that the body melting at  $60^{\circ}$  in part changes to that melting at  $80^{\circ}$  on standing in the cold. The oil which was formed during the oxidation reaction could not be crystallized. It was of a dark-red color and decomposed violently when it was heated. Bromine, in chloroform solution, instantly yielded a yellow, crystalline perbromide. According to the above, the  $\beta$ -phenylhydrazone is to be looked upon as the hydrazo body.  $\alpha$ -Ethylidenephénylhydrazone, melting at  $100^{\circ}$ , does not reduce mercuric oxide in the cold in ethereal solution. It seems to be much more stable when exposed to the air, although the pure  $\beta$ -phenylhydrazone does not decompose rapidly under these conditions. Nitrogen trioxide converts it into the same white, explosive body as is obtained from the  $\beta$ -variety. The ethylidenephénylhydrazones, therefore, display the same relationships as the benzoïn derivatives, and, as in the case of the latter, there are probably three varieties. One marked difference must be noted, however,—the ethylidenephénylhydrazones are readily converted, the one into the other, the one melting at  $60^{\circ}$  into the one melting

<sup>1</sup> Ber. d. chem. Ges., 29, 776.

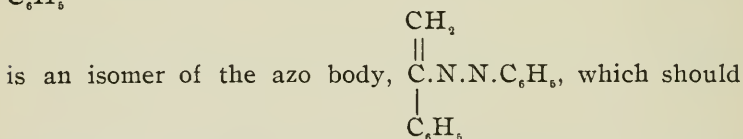
at 80° on standing. The reverse reaction takes place on distilling the  $\alpha$ -body; and the  $\beta$ -variety is changed to the  $\alpha$ -variety, melting at 100°, by simply boiling for a short time with a dilute, alcoholic solution of caustic soda. It is for this reason that an investigation of these substances offers greater difficulties.

*The Action of Phenylhydrazine on  $\alpha$ -Halogen Substitution-products of the Ketones.*

After Nef<sup>1</sup> had shown that the same body which Bender<sup>2</sup> obtained by treating  $\alpha$ -chloracetoacetic ester with phenylhydrazine could also be prepared by the oxidation of the phenylhydrazone of acetoacetic ester by means of mercuric oxide, it seemed necessary to determine if other azo compounds could be prepared according to the same method, and to render the azo structure of benzeneazo- $\beta$ -oxycrotonic acid more certain by means of their study. Hess<sup>3</sup> has already investigated the action of phenylhydrazine on bromacetophenone, obtaining a body which melts at 137°. To this he assigned the formula



as most probable. Accordingly this substance



be obtained by the oxidation of acetophenone. As I mentioned above, I could prepare the product only in the form of an oil, but the behavior of *p*-brombenzeneazo-*i*-styrene, which is crystalline, demonstrates at once that the substance of Hess cannot possibly be an azo body; it has too high a melting-point, and forms no perbromide; in fact, the action of bromine seems to produce a complete decomposition, yielding nothing but tarry products. A molecular weight determination showed that the body has not a simple structure.

<sup>1</sup> Am. Chem. (Liebig), 266, 74.

<sup>2</sup> Ber. d. Chem. Ges. 20, 2747.

<sup>3</sup> Ann. Chem. (Liebig), 232, 234.

Benzene, 27.227.

Depression, 0.075.

Substance, 0.1521.

Calculated for  $2C_{14}H_{13}N_2$ , 418; found, 365.

As this result showed that the body obtained from brom-acetophenone and phenylhydrazine was no azo substance, it was of no further interest to me; nevertheless I will describe a curious reaction which the substance undergoes. Hess's body is decomposed by dilute acids with extreme ease, and a peculiar change takes place. If the pure body is dissolved in warm glacial acetic acid, and then *promptly* precipitated with water, a new body separates in white needles; the greater part, however, remains in solution to be precipitated as an amorphous, brown powder, which could not be purified. If the substance is heated with alcohol and a drop of hydrochloric acid, in a sealed tube at  $100^\circ$  for two hours, there is slight pressure on opening and a little of an amorphous, brown precipitate has separated. If the latter is filtered and the solution evaporated in a vacuum, long, silky needles, melting at  $114^\circ$ – $115^\circ$ , separate. These are identical with those obtained from the solution in acetic acid. Even alcohol alone, without the addition of hydrochloric acid, is able to produce this change if the heating is carried on long enough. In this way I obtained 2 grams of the pure crystals from 7 grams of Hess's body; at the same time a considerable quantity of the brown, amorphous substance is always formed. Analysis of the substance melting at  $114^\circ$ – $115^\circ$  gave the following numbers:

I. 0.1410 gram substance gave 0.4368 gram  $CO_2$ , and 0.0755  $H_2O$ .

II. 0.1638 gram substance gave 0.5036 gram  $CO_2$ , and 0.0907  $H_2O$ .

III. 0.1361 gram substance gave 12 cc. nitrogen at  $22^\circ$  and 738 mm.

	Calculated for $C_{20}H_{18}N_2$ .	I.	Found. II.	III.
C	83.91	84.46	83.84	....
H	6.29	5.95	6.15	....
N	9.78	....	....	9.82

The formula  $C_{20}H_{18}N_2$  is that of the original body with the addition of  $C_6H_6(C_{14}H_{12}N_2 + C_6H_6 = C_{20}H_{18}N_2)$ ,



and the properties of the substance, as well as the melting-point agree closely with those given for desoxybenzoïnphenylhydrazone,<sup>1</sup> but I did not prepare the latter body for comparison. Certainly, the formation of a substance having the formula  $C_{20}H_{18}N_2$  from a substance produced from bromacetophenone and phenylhydrazine is curious. If it is desoxybenzoïnphenylhydrazone the change amounts to a substitution of phenyl for bromine. This reaction deserves further investigation, but as it had no immediate bearing on this work it was, for the present, set aside.<sup>2</sup>

If the body discovered by Hess is dissolved in ether, and dry hydrochloric acid is passed in, a white hydrochloride at once separates. The latter deliquesces in the air and quickly changes to a red, tarry substance. It is soluble in water and addition of alkalis precipitates the same non-crystallizable amorphous substance referred to above. If the hydrochloride is kept in a desiccator it loses a part of its acid and changes to a substance which is stable in the air. This body behaves in the same way when it is treated with alkalis. Benzoyl chloride and acetyl chloride produce crystalline bodies which apparently are identical with the stable hydrochloride. They yield the same amorphous substances when treated with caustic potash or soda and the same change takes place in the original substance if it is treated with the latter reagents. It is evident that Hess's body is very easily decomposed, but the nature of the products formed scarcely invites to further investigation.<sup>3</sup>

<sup>1</sup> Smith and Ransom (This JOURNAL, 16, 111) give  $116^\circ$  as the melting-point of desoxybenzoïnphenylhydrazone, and the melting-point of my body is  $115^\circ$ .

<sup>2</sup> The decomposition described above causes trouble when the product of the action of phenylhydrazine on bromacetophenone is recrystallized from alcohol. It is always partly decomposed by the prolonged boiling necessary to dissolve it, and the decomposition-products are then contaminated with the amorphous substances referred to above. It is best to extract Hess's body three or four times with hot alcohol; the bright, yellow residue is sufficiently pure for further work.

<sup>3</sup> I have improved the method of preparing bromacetophenone as follows: Pure acetophenone is dissolved in pure carbon disulphide, well cooled in a freezing-mixture, and then the calculated quantity of bromine is gradually added, the whole being vigorously stirred, a current of carbon dioxide being passed through the solution in the meantime. This latter precaution is taken in order to remove excess of hydrobromic acid. After all bromine has been added, the solvent is evaporated by gentle heat, *in vacuo*, when the remainder separates as somewhat greenish crystals. The latter are then dissolved in alcohol, and water is added until a separation just begins. The flask is finally placed in a freezing-mixture until crystallization is complete. In order to avoid the intensely irritating odor of bromacetophenone, all of these operations should be carried out in the same vessel.



*The Action of Phenylhydrazine on Chloraldehyde Hydrate.*

The reaction takes place with explosive violence if no diluent is used. In order to obtain the best results, the following method was adopted: 10 grams of chloraldehyde hydrate were dissolved in 200 cc. of alcohol, well cooled, and then 2 gram-molecules of phenylhydrazine slowly added. After a few minutes a separation of phenylhydrazine hydrochloride begins, and finally yellow needles also appear. On standing over night, covered with snow, the whole solidifies to a thick paste. The whole is then filtered and pressed, and finally all traces of phenylhydrazine hydrochloride are removed by repeated trituration by water. The product is then washed with methyl alcohol, dried, and recrystallized from lukewarm alcohol, from which it separates in slightly yellow needles. It is finally dissolved in ether and crystallized *in vacuo*, when it forms colorless prisms, melting at  $94^{\circ}$ – $95^{\circ}$ .

I. 0.1761 gram gave 0.4503 gram  $\text{CO}_2$ , and 0.1034 gram  $\text{H}_2\text{O}$ .

II. 0.1972 gram gave 42 cc. nitrogen at  $19^{\circ}.5$  and 734.5 mm.

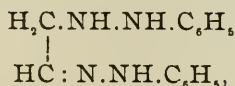
	Calculated for $\text{C}_{14}\text{H}_{16}\text{N}_4$ .	I.	Found.	II.
C	70.00	69.73		....
H	6.66	6.52		....
N	23.33	....		23.66

A molecular weight determination was carried out in solution in benzene.

Benzene	29.2268		
Substance	I. 0.4500	Depression	I. 0.33
"	II. 0.7719	"	II. 0.545

Calculated 240; found I. 229; II. 231.

These results show that the body is the phenylhydrazone of oxyaldehyde



so that no azo body has been produced.

If this phenylhydrazine compound is boiled with alcohol or

benzene, no rapid separation of crystals occurs on cooling, but gradually a mixture is formed which melts all the way from  $95^{\circ}$  to  $110^{\circ}$ . If the mother-liquors are either diluted with water, or evaporated, then there remain some sandy crystals, covered with a thick oil. If these crystals are spread on a porous plate and finally recrystallized from alcohol, they melt at  $160^{\circ}$ – $161^{\circ}$ , and have the same percentage composition as the original body. This substance is probably a polymeric form. If the mixture melting between  $95^{\circ}$  and  $110^{\circ}$  is slowly crystallized from ether, a small quantity of a body melting at  $110^{\circ}$  can be isolated, but the latter changes its melting-point with each recrystallization. Probably the same relationships obtain here as are found in the case of the ethylidene-phenylhydrazones. I have, however, not as yet been able to decide definitely whether there is a third isomeric body, in addition to those melting at  $94^{\circ}$ – $95^{\circ}$  and  $160^{\circ}$ – $161^{\circ}$  respectively. If the variety melting at  $94^{\circ}$ – $95^{\circ}$  is dissolved in alcohol and boiled with phenylhydrazine then, strange to say, no change takes place. If it is heated with pure ether in a sealed tube to  $100^{\circ}$  for two hours, the tube opens without pressure, and all of the crystals are dissolved. On evaporation a thick oil, permeated with crystals melting at  $160^{\circ}$ – $161^{\circ}$ , remains. It is evident that this body is therefore easily converted from one form into the other. Sodium amalgam, in alcoholic solution, reduces it readily, the resulting substance forming long, white needles, melting at  $100^{\circ}$ .

0.2155 gram substance gave 0.5519 gram  $\text{CO}_2$ , and 0.1397 gram  $\text{H}_2\text{O}$ .

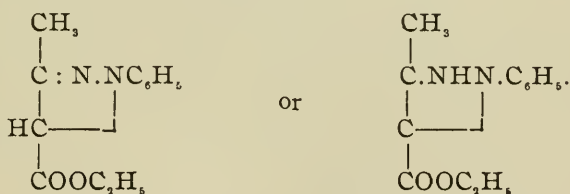
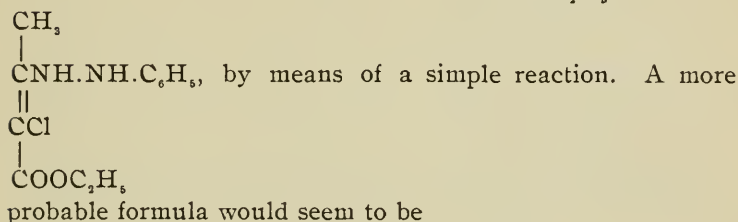
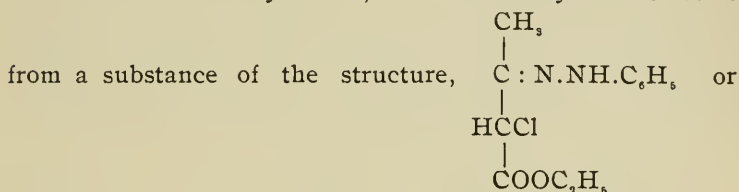
	Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_4$ .	Found.
C	69.40	69.39
H	7.46	7.20

This substance is therefore symmetrical ethylene-diphenylhydrazide,  $\begin{array}{c} \text{CH}_2\text{NHNHC}_6\text{H}_5 \\ | \\ \text{CH}_2\text{NHNHC}_6\text{H}_5 \end{array}$ .

Bender<sup>1</sup> has studied the action of phenylhydrazine on brom- and chlorlaevulinic ester, on brombenzoylacetic ester and on

<sup>1</sup> Ber. d. chem. Ges., 21, 2492.

chloracetone but in none of these cases did he obtain an azo body. The formation of benzeneazo- $\beta$ -oxycrotonic ester from  $\alpha$ -chloracetoacetic ester and phenylhydrazine is, therefore, a solitary instance, if the substance is really an azo body. It is, however, true that the same crystals are obtained by the action of mercuric oxide on the hydrazone of acetoacetic ester, but then, if the constitution assigned to it is really the correct one, a rearrangement of the atoms must have taken place in the case of Bender's synthesis, for an azo body cannot result

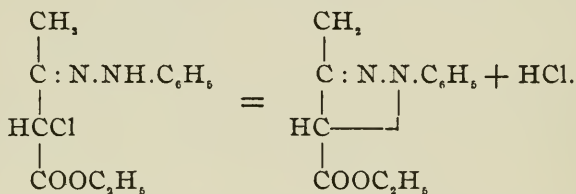


The substance has a simple molecular weight, for I found 206; calculated 218.

The following facts speak against the azo formula: The body melts quietly, without the evolution of a gas; decomposition sets in only considerably above the melting-point. Thiele has shown<sup>1</sup> that his aliphatic azo bodies always give off nitrogen quantitatively when heated above their melting-point, and the same is true of the azo substances described above. Bromine, in chloroform solution, does not give a perbromide,

<sup>1</sup> Ann. Chem. (Liebig), 290, 33.

total decomposition resulting in the formation of a non-crystallizable tar taking place; the body is perfectly stable in the air, if it is in a pure state, while my similar bodies prepared from aliphatic phenylhydrazones are oxidized with explosive violence. The oxidation of the phenylhydrazone of acetoacetic ester by means of yellow oxide of mercury is by no means quantitative; phenylmethylpyrazolone can always be obtained from the alkaline extracts, and the ethereal solution deposits a considerable quantity of a thick oil, in addition to benzene-azo- $\beta$ -oxycrotonic acid. It is scarcely justifiable to draw final conclusions as regards the constitution of the body from such insufficient data. It seems more probable, in view of the facts cited, that Bender's reaction takes place as follows:



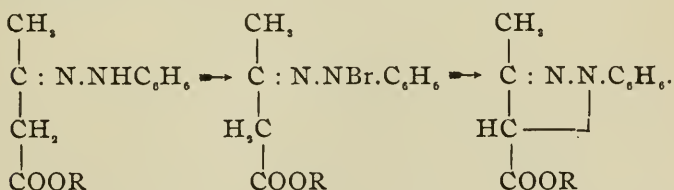
The phenylhydrazone of acetoacetic ester differs markedly in its behavior from the phenylhydrazones of acetone or acetophenone. If it is pure it is not oxidized by the air. 25 grams of the pure, recrystallized hydrazone were covered with petroleum ether and treated exactly as was acetone-*p*-bromphenylhydrazone. After four weeks there was little change. After three months the entire substance had changed to phenylmethylpyrazolone. If the phenylhydrazone of acetoacetic ester

really has the structure  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CNHNHC}_6\text{H}_5 \\ || \\ \text{CH} \\ | \\ \text{COOC}_2\text{H}_5 \end{array}$ , one would expect it

to be oxidized in the air, just as the other compounds of similar constitution are. It is true that the oily or impure crystalline phenylhydrazone does change very rapidly when exposed to the action of the atmosphere, and it is not impossi-

ble that a small quantity of the hydrazo body is present in these preparations, but evidently this question is not easily decided experimentally.

Bromine, in ethereal solution, does not produce the *p*-compound from the phenylhydrazone of acetoacetic ester, as is the case with the other ketone phenylhydrazones. 6 grams of the crystallized phenylhydrazone of acetoacetic ester were dissolved in 100 cc. ether, and then, after cooling, 4.4 grams of bromine were slowly added. At first the bromine color instantly disappears; finally, however, after one-half has been added, the action becomes so slow that two to three hours are necessary to complete it. The ethereal solution is now colored deep-red and a black, tar-like substance has separated. The latter contained hydrobromic acid, but could not be crystallized. The ethereal solution was repeatedly extracted with 10 per cent. caustic potash and finally washed with dilute acids and water, dried over pure sodium sulphate and evaporated. By this method a small amount of a crystalline, red body can be isolated. The latter bears so close a resemblance to the substance discovered by Bender that it could easily be mistaken for it. It melts at  $71^{\circ}$ , however, and contains bromine; most probably it is the *p*-brom derivative of the body described as benzeneazo- $\beta$ -oxycrotonic ester. The formation of this latter substance is much more readily understood if the hydrazone is not given the hydrazo structure:—

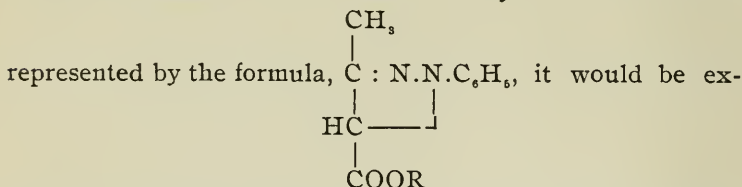


The last compound is then changed into the *p*-brominated body by the action of a further quantity of bromine; and this accounts for the fact that the reaction takes place more slowly toward the end.

In this connection it must be remembered that neither Bender nor Nef was able to reduce the benzeneazo- $\beta$ -oxycro-

tonic ester back to the phenylhydrazone of acetoacetic ester ; they always obtained phenylmethylpyrazolone or bisphenylmethylpyrazolone.

If the substance under discussion really has the structure



pected that reactions which would split the ring could be discovered. Attempts in this direction have, as yet, led to no satisfactory result, because in every such attempt either non-crystallizable tars or derivatives of phenylmethylpyrazolone are formed.

The above considerations show that the azo structure for benzeneazo- $\beta$ -oxycrotonic ester should by no means be taken for granted. On the other hand, this constitution is not disproved, except by negative testimony.

In conclusion, I wish to return hearty thanks to Messrs. Whitsit and Briggs, and to Dr. P. L. Sherman for their continued and ready assistance in this work.

ANN ARBOR, August, 1898.

Contributions from the Chemical Laboratory of the University of California.

## NOTE ON THE ACTION OF LIQUID HYDRIODIC ACID ON ETHYL ETHER.

BY F. G. COTTRELL AND ROY RAYNE ROGERS.

Some time ago, while examining the properties of liquid hydriodic acid,<sup>1</sup> it was noted that when the acid was mixed with ether a vigorous action occurred, the temperature rising rapidly, the mixture, which at first appeared to be homogeneous, separated into two layers, one of which was assumed to be ethyl iodide, judging from its appearance and odor, and the other was assumed to be water and the excess of acid. No attempt was made at the time to separate and purify the product, or to determine the yield. The following supplements the previous work in this particular.

<sup>1</sup> Norris and Cottrell : This JOURNAL, 18, 103 (1896).



The hydriodic acid was prepared and dried according to the method described in the previous paper.<sup>1</sup> The ether was prepared by washing commercial ether with a considerable volume of water, digesting with quicklime for a few days and distilling from the same. This was again distilled and then gave a boiling-point constant within a tenth of a degree.

After several preliminary experiments the following form of apparatus was adopted. We believe it will be found a very convenient form for reactions which are to be carried out under pressure.

The sealed end of a straight eudiometer-tube provided with a glass stop-cock was cut off and a smaller tube, sealed at one end, introduced into it, open end first. The cut end of the large tube was then sealed, thus providing a vessel of two chambers, into each of which liquids could be introduced through the stop-cock.

The whole apparatus was now weighed, the tube was then surrounded with solid carbon dioxide and gaseous hydriodic acid conducted by means of a narrow delivery-tube to the bottom of the eudiometer-tube, where it condensed to a liquid surrounding the inner tube. When about 15 cc. of this liquid had been collected, the delivery tube was withdrawn and the acid cooled until it solidified. Then a weighed amount of ether was run into the inner tube, and the stopcock closed and tied in securely.

The apparatus was now tipped slightly so that the ether mixed in small quantities at a time with the acid. The ether on coming in contact with the solid acid produced a vigorous reaction. The latter melted rapidly, even while surrounded by the solid carbon dioxide. If the ether and acid are suddenly mixed the temperature will rise from the freezing-point of the acid ( $-55^{\circ}$  C.) to at least  $+40^{\circ}$  or  $50^{\circ}$ . When mixing was complete the whole apparatus was weighed to determine the weight of acid used.

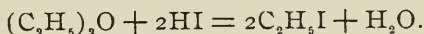
During the mixing the products began to separate into two layers. The tube was set aside for a week in a dark place average temperature about  $18^{\circ}$ ), at the end of which time

<sup>1</sup> *Loc. cit.*

the heavier of the two layers had relatively increased in volume. After being cooled down somewhat, the tube was opened. Water was added, which mixed with the upper layer, but would not mix with the lower. The lower layer was washed with water, then with a little weak solution of caustic potash, dried over calcium chloride, and distilled twice. The following are the numerical data :

	Grams.
Weight of ether used	8.91
Weight of acid used	42.30

This is 1.33 times the quantity of acid required by theory for the reaction :



Weight of crude product after washing with water, 35 grams ; this is 94 per cent. of the quantity required by theory.

Weight of product after first distillation, 32.8 grams, which is 88 per cent. of the quantity required by theory.

After the second distillation the whole of the material boiled between  $71.9^\circ$  and  $72^\circ$  under 756 mm. pressure. The boiling-point of ethyl iodide, given by different authorities,<sup>1</sup> ranges about a degree on each side of this. Its specific gravity at  $18^\circ$  referred to water at the same temperature was found to be 1.941. Hagen gives 1.935 at  $20^\circ$ , and Linnemann 1.944 at  $14.5^\circ$ .<sup>2</sup> Its refractive index for the *D* line was 1.5133 at  $18.5^\circ$ . Hagen<sup>3</sup> gives 1.5131 at  $20^\circ$ .

Silva<sup>4</sup> found that when gaseous hydriodic acid reacted on methyl ether at  $0^\circ$  to  $4^\circ$ , the whole of the ether was converted into methyl iodide. With ethyl ether, on the contrary, only part was converted into iodide and part into alcohol ; and the same was true for the higher ethers. No quantitative data are given.

The formation of water by the reaction itself in such cases as the above, soon establishes the same condition as when using a concentrated aqueous solution of the acid. It would be interesting to study the behavior of the anhydrous acid in

<sup>1</sup> Landolt and Börnstein : Chem. Phys. Tab. 1894, p. 65.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.* p. 427.

<sup>4</sup> Compt. rend., 81, 323 (1875).

reactions where no water can form; *e. g.*, in the addition of hydrogen to benzene (Cf. Berthelot).<sup>1</sup>

It seems not improbable from the rapid and widespread increase in our facilities for liquefying and handling considerable quantities of gases that this method of applying such reagents as chlorine, sulphur dioxide, and ammonia may eventually come into quite general use. It has the great advantage of permitting a high concentration of the reagent without the necessity of introducing water or other solvents, while its practical application is by no means as difficult as might at first be supposed.

BERKELEY, CAL., Sept., 1898.

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## CONTRIBUTIONS TO OUR KNOWLEDGE OF THE OIL OF LEMON-GRASS.<sup>2</sup>

BY WILH. STIEHL.

The question in regard to the composition of the oil of lemon-grass has of late become of special interest, on account of the relations between the aliphatic aldehydes,  $C_{10}H_{16}O$ , (or their condensation-products with acetone) contained in them, and the ketones,  $C_{13}H_{22}O$ , obtained from violets.

Oil of lemon-grass or Indian oil of verbena is, as is well known, obtained by distillation of a species of grass, *Andropogon citratus*, in British India, Ceylon, Singapore, and Java, and is there sold in original packages to the European importers.

Messrs. Ph. Barbier and L. Bouveault deserve special mention for their excellent work in the investigation of the constituents of the oil of lemon-grass. Schimmel & Co., of Leipsic, have put on the market, under the name of "citral," an inactive aldehyde,  $C_{10}H_{16}O$ , obtained from oil of lemon-grass, without, however, stating how it is isolated and without carefully investigating it. F. D. Dodge<sup>3</sup> first described a method for the isolation of a characteristic aldehyde,  $C_{10}H_{16}O$ , from oil of lemon-grass. He shook the oil with a warm solution of sodium bisulphite, and in a short time obtained a solid bisul-

<sup>1</sup> J. prakt. Chem., 104, 106 (1868).

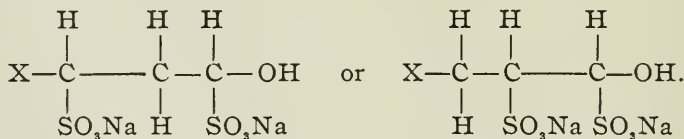
<sup>2</sup> Communicated by the Author in MS. in German.

<sup>3</sup> This JOURNAL, 12, 555.

phite compound. In a few hours this became liquid again, and there were thus obtained an aqueous liquid and an oil floating upon this. Dodge did not further investigate the oil. He treated the aqueous solution with caustic soda, and obtained a substance,  $C_{10}H_{16}O$ , which he investigated, and, after identification, called "citriodoric aldehyde." On the other hand, he evaporated the aqueous solution containing the aldehyde and bisulphite, and obtained from it beautiful crystals an inch in length, which had the composition  $C_{10}H_{16}O \cdot 2NaHSO_3 + 4Na_2SO_3 + 50H_2O$ . These gave citriodoric aldehyde with caustic soda.

Dodge properly drew the conclusion that the bisulphite compound of citriodoric aldehyde conducts itself quite differently from the typical compounds of the aldehydes with bisulphite. Dodge himself sums up his further investigation by saying that oil of lemon-grass contains an aliphatic aldehyde,  $C_{10}H_{16}O$ , with two ethylene bonds, which can easily be converted into cymene.

It may here be mentioned that Fr. Heusler<sup>1</sup> has observed a similar behavior in the case of the bisulphite compound of cinnamic aldehyde, and from the water solution has isolated the compound,  $C_6H_5 \cdot C_2H_3(SO_3Na)CH(OH)(SO_3Na)$ . From this compound, or its solution in water, cinnamic aldehyde can be separated only by means of caustic alkalies. This behavior is perhaps connected with the presence of the group  $X-CH:CH \cdot CHO$ , and the formation of the soluble bisulphite compound may take place in either of the two ways indicated below:



According to this view citriodoric aldehyde must be  $C_7H_{13} \cdot CH:CH \cdot CHO$ , analogous to cinnamic aldehyde,  $C_6H_5 \cdot CH:CH \cdot CHO$ .

Then W. Semmler<sup>2</sup> investigated the citral which Schimmel

<sup>1</sup> Ber. d. chem. Ges., 24, 1805.

<sup>2</sup> *Ibid.*, 24, 201-211.

& Co. put on the market, and declared it to be identical with the geranial obtained by him by oxidizing "geraniol" so that the two expressions have been used since that time to designate one and the same substance.

Further, R. Hefelmann<sup>1</sup> made a quantitative estimation of geranial in oil of lemon-grass free from terpenes, and succeeded by means of bisulphite in isolating 13 per cent. of an aldehyde identical with geranial. Ferd. Tiemann and W. Semmler<sup>2</sup> have also worked on geranial and citral in their investigations on irone and ionone, and state that citral can be separated from oil of lemon-grass by means of the easily crystallized compound with sodium bisulphite, and that the compound of geranial and bisulphite in contact with the liquid from which it is formed passes into solution if the temperature is not too low, but that the aldehyde cannot be separated either by alkali carbonates or by caustic alkalies, as the sodium salt of a true sulphonic acid is formed.

This is a different behavior from that observed by Dodge<sup>3</sup> in the case of citriodoric aldehyde, and is more like that of the typical compounds of aldehydes with bisulphite. Accordingly, geranial (citral) cannot contain the group  $X-CH:CH.CHO$ , but must contain this,  $X-CH_2.CH_2-CHO$ .

It is clear, therefore, that up to the present two aldehydes of the formula  $C_{10}H_{16}O$  have been shown to be present in oil of lemon-grass; *viz.*, Dodge's citriodoric aldehyde,  $C_7H_{11}.CH:CH.CHO$ , and Semmler's geranial (citral),  $C_7H_{11}.CH_2.CH_2.CHO$ .

The formula proposed by F. Tiemann and W. Semmler for geranial cannot be correct, for the different conduct of citriodoric aldehyde and citral towards sodium bisulphite cannot be explained by means of it.

Next, O. Doebner<sup>4</sup> applied his synthesis of  $\alpha$ -alkyl- $\beta$ -naphthocinchoninic acids from aldehydes, pyrrolic acid and  $\beta$ -naphthylamine to the terpene aldehydes, and describes  $\alpha$ -citronellal- $\beta$ -naphthocinchoninic acid melting at  $225^\circ$  and  $\alpha$ -citral- $\beta$ -naphthocinchoninic acid melting at  $197^\circ$ .

<sup>1</sup> Chem. Centralblatt, 64, (I) 45 (1894).

<sup>2</sup> Ber. d. chem. Ges., 26, 2708-2729.

<sup>3</sup> This JOURNAL, 12, 553-564.

<sup>4</sup> *Ibid.*, 27, 2020-2030.



Döbner tries at first to use this synthesis for the quantitative estimation of aldehydes in natural ethereal oils, but his efforts are unsuccessful, first, because the reaction does not take place quantitatively, and secondly, because an excess of pyroracemic acid and  $\beta$ -naphthylamine causes the formation of  $\alpha$ -methyl- $\beta$ -naphthocinchoninic acid, which remains mixed with the corresponding  $\beta$ -naphthocinchoninic acid. In an attempt to apply his reaction directly to oil of lemons, Doebner finds in this oil about 8 per cent. of aldehydes, consisting of about 25 per cent. citral and 75 per cent. citronellal.

Later, Ph. Barbier and L. Bouveault<sup>1</sup> show that oil of lemons contains no citronellal,  $C_{10}H_{18}O$ , but that it does contain dextro-licarhodol,  $C_{10}H_{16}O$ .

In the meantime Ph. Barbier and L. Bouveault<sup>1</sup> published their careful investigations on the constituents of oil of lemon-grass, and I give here a brief résumé of these.

They confirm Dodge's discovery<sup>2</sup> of citriodoric aldehyde in oil of lemon-grass. To obtain this aldehyde, they distilled five times under diminished pressure very carefully a sufficient quantity of the oil of lemon-grass and obtained the following three principal fractions :

I.  $65^{\circ}$ – $75^{\circ}$  under 12 mm. pressure ( $170^{\circ}$ – $175^{\circ}$  at ordinary pressure).

II.  $110^{\circ}$ – $115^{\circ}$  under 12 mm. pressure (citriodoric aldehyde).

III. Above  $115^{\circ}$  under 12 mm. pressure (residue not investigated).

In fraction I. they found, besides a terpene (probably limonene), principally methylheptenone,  $C_8H_{14}O$ , for which they propose the formula,  $CH_3-C(CH_3)=CH-CH_2-CH_2-CO-CH_3$ , to account for the products of oxidation.

In fraction II. the citriodoric aldehyde of Dodge must be contained. As meanwhile the papers of Tiemann and Semmler on geranial and citral from oil of lemon-grass appeared, and as it seemed not improbable that geranial and citriodoric aldehyde might be identical, Ph. Barbier and L. Bouveault<sup>3</sup> tested the formula which was proposed by Tie-

<sup>1</sup> Compt. rend., 118, 953-986, 1050-1052; 121, 1159-1162; 122, 84-86, 393-395, 1422-1424.

<sup>2</sup> This JOURNAL, 12, 553.

<sup>3</sup> Compt. rend., 118, 953-986, 1050-1052.



mann for geranial. They found that this could not possibly be the formula of their citriodoric aldehyde, and therefore they gave this another formula, which accounted for the products of decomposition.

In order to learn more about this interesting compound, and to continue further their investigations on the aldehydes,  $C_{10}H_{16}O$ , obtained from the alcohols,  $C_{10}H_{18}O$ , they compared the former with the aldehyde contained in oil of lemon-grass. For this purpose they studied the semi-carbazones<sup>1</sup> of these aldehydes exhaustively.

They again carefully distilled the above fraction II. in a vacuum with the aid of a column-still attachment, and separated it into the following fractions :

I.  $107^{\circ}$ – $110^{\circ}$  under 10 mm. pressure.

II.  $110^{\circ}$ – $112^{\circ}$  under 10 mm. pressure.

On crystallizing the semi-carbazones of these two fractions they obtained from both three different semi-carbazones melting at  $171^{\circ}$ ,  $160^{\circ}$ , and  $135^{\circ}$ . They then prove in an elegant manner that the isomerism of these three semi-carbazones cannot be referred to the nitrogen, as they can all be converted into one semi-carbazone melting at  $135^{\circ}$ .

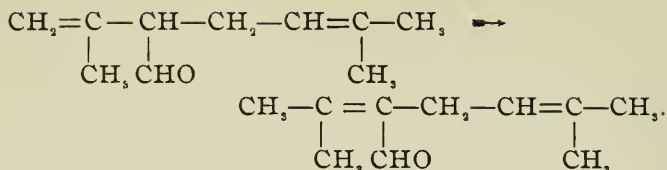
They say further : "Il n'existe pas dans l'essence de Lémon-gras d'aldéhyde répondant à la formule  $C_{10}H_{16}O$ , car il ne se forme pas de semi-carbazones autre que celles que nous venons de décrire." For two of the three aldehydes,  $C_{10}H_{16}O$ , they propose formulas, and call one "aldéhyde instable" and the other "aldéhyde stable." They also formulate their easy conversion into cymene.

In a later article :<sup>2</sup> "Sur les aldéhydes dérivées des alcools  $C_{10}H_{18}O$  isomériques" they complete their investigations and prove that the semi-carbazone melting at  $171^{\circ}$  belongs to licarhodal, and that this under the influence of sulphuric acid passes into lemonal, as they call the aldehyde,  $C_{10}H_{16}O$ , which yields a semi-carbazone melting at  $135^{\circ}$ .

The conversion of licarhodal into lemonal they represent as analogous to the conversion of eugenol into isoeugenol, of safrol into isosafrol, and of estragol into anethol as follows :

<sup>1</sup> Compt. rend., 121, 1159–1162.

<sup>2</sup> *Ibid.*, 122, 84–86.

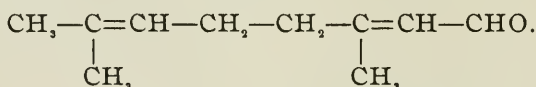


In connection with this subject they say : "La transformation du licarhodol en lémonal n'est pas réversible, et le licarhodol, qui se rencontre dans les produits d'oxydation du lémonal naturel (géraniol) de l'essence d'*Andropogon schoenanthus* provient du licarhodol gauche dans cette essence."

They have further investigated the citral from oil of lemons, and found that three aldehydes,  $\text{C}_{10}\text{H}_{16}\text{O}$ , occur in it, whose semi-carbazones melt at  $171^\circ$ ,  $160^\circ$ , and  $135^\circ$ , and they remark : "Le citral de l'essence de citron ne contient donc pas de citronellal et la combinaison naphthocinchonique décrite par M. Doebner comme dérivant du citronellal et sans doute celle qui correspond au licarhodol."

It will be seen, therefore, that according to Barbier and Bouveault citronellel,  $\text{C}_{10}\text{H}_{18}\text{O}$ , cannot be contained either in oil of lemon-grass or in oil of lemons. In addition to the inactive aldehydes,  $\text{C}_{10}\text{H}_{18}\text{O}$ , geranial (citral) and citriodoric aldehyde, there is, however, an inactive aldehyde,  $\text{C}_{10}\text{H}_{16}\text{O}$ , laevo-licarhodol contained in the oil. The detection and isolation of these aldehydes are difficult because, under the influence of acid reagents, they are transformed into the most stable inactive compound.

In a still later communication<sup>1</sup> these investigators give additional evidence of the existence of the three aldehydes,  $\text{C}_{10}\text{H}_{16}\text{O}$ , in oil of lemon grass, and propose for one of these, lemonal, the following formula :



Their parallel investigations of the alcohols,  $\text{C}_{10}\text{H}_{18}\text{O}$ , I can only mention here.

Recently F. Tiemann<sup>2</sup> has again published the results of

<sup>1</sup> Compt. rend., **122**, 842-844.

<sup>2</sup> Ber. d. chem. Ges., **31**, 820.

his investigations on the constitution and the chemical conduct of geranial (citral) without, however, saying much that is new. He mentions among other things the splitting of citral into acetic aldehyde and methylheptenone by means of a solution of potassium carbonate which was effected by A. Verley, and recommends Doebner's  $\alpha$ -citryl- $\beta$ -naphthochinchonic acid (of melting-point  $197^{\circ}$ ) as a means of detecting and characterizing citral.

On the other hand, I cannot accept Tiemann and Krüger's proof that only geranial is contained in the oil of lemon-grass, and that its semi-carbazone can be resolved into isomeric substances that melt between  $130^{\circ}$  and  $171^{\circ}$ . On the contrary, on the basis of my experiments, an account of which is given below, I can fully confirm the statement of Ph. Barbier and L. Bouveault, for perfectly pure inactive citral (geranial) never gives a semi-carbazone melting at  $171^{\circ}$ , as O. Wallach and W. Naschold<sup>1</sup> have also found.

Notwithstanding the fact that Ph. Barbier and L. Bouveault have fully established the presence of three aldehydes,  $C_{10}H_{16}O$ , in oil of lemon-grass, and that these investigators have just as certainly proved the absence of citronellal from oil of lemon-grass as well as from oil of lemons, the following passage, nevertheless, occurs in this article: "Citral ist bislang der einzige Terpenaldehyd, von der Formel  $C_{10}H_{16}O$ , welcher in ätherischen Oelen nachgewiesen worden ist. Neben demselben tritt nur sein Dihydroderivat, das Citronellal zuweilen unter den Produkten des pflanzlichen Stoffwechsels auf. O. Doebner hat auf diesen Thatbestand zuerst aufmerksam gemacht, und auch angegeben, wie man Citronellal neben Citral nachweisen kann."<sup>1</sup>

In this article F. Tiemann also states that the condensation of geranial with acetone, according to Claisen, furnishes an excellent method for detecting and sharply characterizing this aldehyde,  $C_{10}H_{16}O$ , in the form of pseudoionone, provided

<sup>1</sup> Ber. d. chem. Ges., 31, 822. In spite of the work of Barbier and Bouveault, O. Doebner (Ber. d. chem. Ges., 31, 1891) recently expresses the opinion that citronellal is contained in oil of lemon-grass. This, as well as other errors in Doebner's article, is sufficiently explained by the work described in the present communication so that the work of Doebner, which only came to my knowledge after I had completed the preparation of this article, is refuted by the latter. I shall, in another place, return to the numerous contradictory statements of Doebner.

secondary reactions are avoided. He describes a method of procedure for this general method, by means of which geranial can be detected in oil of lemon-grass with ease. I have also been led, independently of F. Tiemann, to this excellent method of detecting the aldehydes,  $C_{10}H_{16}O$ , in the ethereal oils, and can confirm the statement that pseudoionone is always obtained, whenever geranial or citral is contained in the original material. For this reason I have made this method, the application of which I shall describe farther on, the foundation of my investigation of the oil of lemon-grass.

As the condensation of the whole of the aldehyde contained in natural oil of lemon-grass with acetone gave me a mixture of aldehyde-acetone condensation-products, in which I could, to be sure, detect Tiemann's pseudoionone, but from which I could not isolate it in pure condition, I decided to separate the aldehydes, the presence of which had been shown by the previous investigations of Dodge, Barbier and Bouveault, and Tiemann and Semmler.

#### I. *Investigation of Oil of Lemon-grass.*

Large quantities of directly imported, unadulterated oil of lemon-grass were well mixed, and in portions of 50 kilograms carefully separated by water-vapor in an apparatus fitted with a column-still attachment into fractions of  $2-2\frac{1}{2}$  kilograms.

##### A.

20 fractions of 50 kg.

I.	$\alpha_D$ for 1 dm.	= +	$10^{\circ}51'$
IV.	" " "	= +	$7^{\circ}45'$
VII.	" " "	= +	$0^{\circ}41'$
IX.	" " "	= -	$0^{\circ}40'$
XIII.	" " "	= -	$1^{\circ}0'$
XVII.	" " "	= -	$1^{\circ}30'$
XX.	" " "	= -	$2^{\circ}5'$

##### B.

25 fractions of 50 kg.

I.	$\alpha_D$ for 1 dm.	= -	$23^{\circ}0'$
III.	" " "	= -	$15^{\circ}15'$
X.	" " "	= -	$1^{\circ}13'$
XIII.	" " "	= -	$0^{\circ}50'$
XVII.	" " "	= -	$1^{\circ}45'$
XXII.	" " "	= -	$2^{\circ}45'$
XXV.	" " "	= -	$2^{\circ}50'$

I have here given the results of these two distillations for the reason that they show that oil of lemon-grass from different sources sometimes contains dextro-rotatory, sometimes laevo-rotatory, hydrocarbons, and that the less volatile active aldehydes are always laevo-rotatory, as I shall show later. A transition from active terpenes through inactive aldehydes to active aldehydes, therefore, takes place.

From the first fractions, besides cymene, which is probably formed by elimination of water from the aldehydes,  $C_{10}H_{16}O$ , only limonene and dipentene could be isolated, the latter being characterized by means of its bromide melting at  $126^{\circ}$ .

Thereupon geraniol and citronellal were sought for in the fractions, but neither was found in the oils examined by me.

The other fractions of the oil of lemon-grass were then subjected to careful, repeated fractionations under diminished pressure and divided into the following principal fractions:

Fraction.	A.	B.	C.
Boiling pt. 12 mm.	106-108°	117-120°	126-135°
“ “ 760 “	226-229°	133-137°	240-245°
Density at 20° D =	0.8928	0.9020	0.8980
Refract. at 20° $n_D$ =	1.48451	1.48905	1.48050
Rotation in 1 dm. tube $\alpha_D$	$-\frac{1}{2}^{\circ}$	$-5^{\circ}6'$	$-10\frac{1}{2}^{\circ}$

As the  $\alpha$ -citryl- $\beta$ -naphthocinchoninic acid melting at  $197^{\circ}$  is especially characteristic of geranial (citral), I prepared the naphthocinchoninic acid compounds of the above fractions according to O. Doebner's directions, and obtained the following results:

Fraction *A* contains only very small quantities of geranial; for the melting-point of the naphthocinchoninic acid prepared from it ranges from  $197^{\circ}$  to  $205^{\circ}$ , and the acid can be separated into (*a*) a difficultly soluble portion melting at  $197^{\circ}$ , and (*b*) an easily soluble portion melting at  $204^{\circ}$ - $205^{\circ}$ .

Fraction *B* contains no geranial and gives the following two naphthocinchoninic acids: (*a*) a difficultly soluble one melting at  $205^{\circ}$ , and (*b*) an easily soluble one melting at  $229^{\circ}$ .

Finally, fraction *C* gives only one naphthocinchoninic acid, and this melts at  $244^{\circ}$ - $246^{\circ}$ .

It will be seen from the results of the methodical fractiona-



tion of natural oil of lemon-grass, that several aldehydes must be present in it, as several easily distinguished  $\alpha$ -alkyl- $\beta$ -naphthocinchonic acids were obtained, and that even a carefully distilled oil of lemon-grass (citral commerciale<sup>1</sup>) can never be claimed to be citral (geranial).

As no homogenous substances can be obtained by distillation, I have been obliged to seek for other methods of separation.

## II. *Separation of the Aldehydes of Oil of Lemon-grass by means of Sodium Bisulphite.*

In order, at the outset, to exclude all terpenes and other substances that are not aldehydes (methylheptenone was not present in the oil worked up by me), I separated the aldehydes of oil of lemon-grass by means of sodium bisulphite as follows:

10 kilograms of fine oil of lemon-grass, 20 kilograms of a 35 per cent. solution of sodium bisulphite, and 10 kilograms of ice were stirred together until the solid bisulphite compound was formed, then this was at once filtered cold by means of a pump, well washed out, and pressed to hard cakes in a well-cooled press. These cakes were then broken up in ice-water and decomposed by stirring them with a solution of sodium carbonate. The oil thus obtained was carefully washed and rectified with water-vapor or in a vacuum. The mixture of aldehydes had the following properties:

Boiling-point	106°-128° under 12 mm. pressure;
	225°-243° " 758 " "
Density	0.8887 at 20°;
Refraction $n_D$	= 1.48306 at 20°;
Rotation $\alpha_D$	= -4° 13' at 20° in a 1 dm. tube.

A mixture of aldehydes having the above properties was called "citral," because it was obtained from oil of lemon-grass through the pure double compound with sodium bisulphite. But this is absolutely inadmissible, as citral (geranial) in the first place is optically inactive, and, further, it has a sharp, constant boiling-point and other well-marked properties.

<sup>1</sup> This expression has been introduced by a French firm.



By fractionating this mixture I then obtained almost exactly the same fractions that I obtained from oil of lemon-grass and designated as *A*, *B*, and *C*; and these gave entirely similar  $\alpha$ -alkyl- $\beta$ -naphthocinchoninic acids. Besides these I obtained a portion boiling at  $140^{\circ}$ – $145^{\circ}$  under 12 mm. pressure, which showed a rotation of  $\alpha_D = -26^{\circ}$  in a 100 mm. tube, gave a naphthocinchoninic acid melting at  $251^{\circ}$ – $252^{\circ}$ , and had markedly the odor of cedar wood.

As I could not obtain pure geranial (citral) in this way, I made it by oxidation of geraniol which had been purified with the aid of its compound with calcium chloride according to the method of W. Semmler.<sup>1</sup> The geranial (citral) purified through the bisulphite compound had the following physical properties:

Boiling-point:  $111^{\circ}$ – $112^{\circ}$  under 12 mm. pressure;  
 "  $214^{\circ}$ – $227^{\circ}$  " 760 " "  
 Density: 0.8898 at  $20^{\circ}$ ;  
 Refraction:  $n_D = 1.48752$  at  $20^{\circ}$ ;  
 Rotation:  $\alpha_D = \pm 0^{\circ}$  (inactive).

This is therefore undoubtedly the geranial (citral) of Tiemann and Semmler. The melting-point of the naphthocinchoninic acid is  $197^{\circ}$ .

As Tiemann and Semmler<sup>2</sup> have called attention to a peculiar behavior of the bisulphite compound of citral on standing longer than twenty-four hours in the liquid in which it is formed, and as Dodge<sup>3</sup> had previously observed a no less peculiar behavior of the bisulphite compound of citriodoric aldehyde under the same conditions, which was entirely different from that of the citral bisulphite, I first performed the following experiments: On the one hand I shook one part geranial, and, on the other hand, one part of the above mixture of aldehydes with two parts of a 35 per cent. solution of bisulphite, and two parts water until the solid bisulphite compound was formed. During the stage of formation no difference between the two cases was observed. The two masses were then allowed to stand. After the lapse of an hour the bisulphite compound of the aldehydes from oil of lemon-grass be-

<sup>1</sup> Ber. d. chem. Ges., **23**, 2965; **24**, 201; **26**, 2708.

<sup>2</sup> *Ibid.*, **26**, 2708.

<sup>3</sup> This JOURNAL, **12**, 553–564.

gan to liquefy and became markedly warm, while the compound of geranial remained solid. After a time the bisulphite compound of the aldehyde of lemon-grass was decomposed, with the exception of a small residue of little leaf-like crystals, into an oil and a clear aqueous solution with an alkaline reaction. This geranial bisulphite, which was at first granular, had become converted into beautiful laminae of a silken lustre in twenty-four hours. The small quantity of aqueous liquid that separated during this time still retained an acid reaction.

Thereupon I repeated these experiments, and warmed the bisulphite compounds in their mother-liquors about a quarter of an hour in a boiling water-bath, and then found that both had become liquid, but from the bisulphite compound from oil of lemon-grass an oil had separated, which was not the case with the geranial bisulphite.

I then carefully cooled both, when the geranial bisulphite crystallized out, but the bisulphite compound from the oil of lemon-grass did not. I then separated the oil from the latter, and filtered the aqueous solution from the former. I then extracted both aqueous solutions with ether and treated them with sodium bicarbonate. In neither case did I observe any separation at all. I then added caustic soda to both, and obtained from the solution of the aldehydes of the oil of lemon-grass an abundant yield of oil, while the bisulphite solution of the geranial gave nothing. This caused me to repeat the experiments of F. D. Dodge,<sup>1</sup> and of Tiemann and Semmler.<sup>2</sup> For the preparation of citriodoric aldehyde, according to Dodge, one kilogram of the above mixture of aldehydes of natural oil of lemon-grass was shaken with two kilograms of the solution of commercial sodium bisulphite, and two kilograms of water, at the ordinary temperature, until a bisulphite compound was formed which caused the entire mass to solidify, and then this was further shaken until it became liquid again. In this way an oil floating upon the surface was obtained and an aqueous clear solution. The oil was separated and placed aside, while the aqueous solution was

<sup>1</sup> This JOURNAL, 12, 553.

<sup>2</sup> Ber. d. chem. Ges., 26, 2709; 24, 203; 31, 820.

digested with sodium bicarbonate at  $40^{\circ}$ – $50^{\circ}$ , and then extracted with ether. The aqueous solution after treatment with ether was shaken with concentrated caustic soda in the cold. The oil, which separated in large quantities, was well washed and rectified with water-vapor or in a vacuum. In this way the perfectly inactive citriodoric aldehyde of F. D. Dodge was obtained.

On the other hand, I also attempted the preparation of citral (geranial) according to the directions of F. Tiemann and W. Semmler, and I observed that, in the first place, the geranial bisulphite also dissolves if allowed to stand for some time in the liquid in which it is formed, and that after this it cannot be regenerated by caustic soda; and that, in the second place, a sufficient quantity of a strongly acid solution of sodium bisulphite must be used in order that geranial (citral) may be formed from the natural aldehydes of lemon-grass under the transforming influence of sulphurous acid. Therefore each portion of one kilogram of the mixed aldehydes of the oil of lemon-grass was thoroughly shaken with four kilograms sodium bisulphite and two kilograms water until the bisulphite compound was formed. The temperature was then raised to  $40^{\circ}$ – $50^{\circ}$ , then again cooled, and then allowed to stand in a cool place for twenty-four hours. The beautifully crystallized geranial bisulphite was then drawn off, by means of a pump, from the aqueous solution and the accompanying oil, or separated from them by careful washing with alcohol and ether. The geranial bisulphite was then decomposed at a low temperature by means of sodium carbonate. The product obtained is the citral of Tiemann and Semmler, which, I have convinced myself, is identical with the geranial from geraniol. It should be mentioned that, after the digestion with sodium carbonate at  $40^{\circ}$ – $50^{\circ}$ , and after the subsequent extraction with ether, I separated the citriodoric aldehyde from the aqueous solution by means of caustic soda.

The analyses and constants of geranial are given in the table farther on.

Finally, I sought for the laevo-licarhodal which was pre-

pared by Barbier and Bouveault<sup>1</sup> by the aid of its semicarbazone melting at  $171^{\circ}$ , and I found that this compound was contained in the oil that was set aside in the course of the preparation of citriodoric aldehyde and of geranial. I have called this aldehyde allo-lemonal and have separated it by the following method by means of sodium bisulphite directly from oil of lemon-grass.

The conditions may be so chosen that the citriodoric aldehyde passes into solution in the form of the bisulphite compound which can be decomposed only by caustic soda; the geranial dissolves as a sulphonic acid which cannot be regenerated, while the bisulphite compound of allo-lemonal decomposes, yielding allo-lemonal; or the conditions may be so chosen that citriodoric aldehyde remains in solution, geranial being present at the same time in the form of a solid bisulphite compound, and allo-lemonal as an oil, under which circumstances they can be separated.

One kilogram of the mixed aldehydes of oil of lemon-grass was shaken with two kilograms sodium bisulphite and two kilograms water, until a solid bisulphite compound was formed, and then immediately shaken further until solution or decomposition of this compound was brought about. In consequence of the great heat of reaction which is evolved in the formation of the soluble bisulphite compound of citriodoric aldehyde,  $C_{10}H_{16}O \cdot 2NaHSO_3$ , any geranial which was present remained dissolved as sulphonic acid, while the allo-lemonal separated. At this temperature the allo-lemonal is reduced to a considerable extent to allo-lemonol by the action of the sulphurous acid, while geranial and citriodoric aldehyde do not suffer this change. Therefore, 250 grams of the crude allo-lemonal were shaken with 500 grams sodium bisulphite and 500 grams water until the solid bisulphite compound was formed, then well cooled, and the solid compound drawn off by means of a pump, and washed with alcohol and ether. The bisulphite compound of allo-lemonal is now added either to a cold dilute solution of sodium carbonate or to pure warm water, when pure allo-lemonal separates easily, and can be rectified

<sup>1</sup> Compt. rend., 122, 84-86.

either in steam or under diminished pressure. The aldehyde obtained in this way is optically active, and according to the analyses and determination of its molecular weight it has the formula  $C_{10}H_{18}O$ . It is the laevo-licarhodol of Barbier.

The physical constants and the conduct towards bisulphite I have given in the table which will be found farther on.

Barbier and Bouveault carried out their beautiful investigations on the aldehydes of the oil of lemon-grass with the aid of their semicarbazones; and although O. Wallach and W. Naschold<sup>1</sup> have shown that many of these occur in two isomeric forms, comparable results must be obtained in working according to one and the same method under definite conditions. Therefore, we convert our three aldehydes, citriodoric aldehyde, geranial, and allo-lemonal, into semicarbazones according to the following method:

A solution of semicarbazide was prepared according to the directions of Thiele and Stange<sup>2</sup> from 130 grams hydrazine sulphate, 55 grams sodium carbonate, 85 grams sodium cyanate, and 1000 cc. water. This solution, in portions of 100 cc., was treated with 150 cc. alcohol, filtered after standing for several hours, and 10 grams of the aldehyde added to the clear solution. After some time the separation of the semicarbazone began and in twenty-four hours the greater part of it had crystallized out. The filtered alcoholic solution was precipitated with water and the semicarbazone thus obtained also recrystallized from alcohol. The combined semicarbazones were then recrystallized once from methyl alcohol with the addition of water, and gave the semicarbazones that were used in determining the melting-points. The results will be found in the table.

Thereupon the  $\alpha$ -alkyl- $\beta$ -naphthocinchoninic acids of O. Doebner<sup>3</sup> were prepared from the three aldehydes in the following manner: 10 grams aldehyde, 6 grams pyrrolacemic acid, and 10 grams  $\beta$ -naphthylamine were boiled for about three hours in solution in absolute alcohol and the  $\alpha$ -alkyl- $\beta$ -

<sup>1</sup> Ber. d. chem. Ges., 28, 1957.

<sup>2</sup> Ann. Chem. (Liebig), 281, 19.

<sup>3</sup> Ber. d. chem. Ges., 27, 2026.



naphthocinchoninic acids recrystallized once from absolutely anhydrous alcohol and used for the determination of the melting-points and for analyses. The results are included in the table already referred to.

The condensation of the three aldehydes with acetone was effected according to the following general method which excludes secondary reactions. Precaution must be taken to avoid these latter as they are apt to take the lead, as is shown by the example which is quoted in the well-known Ionone Patent.<sup>1</sup>

Fifty-gram portions of well dried and freshly distilled aldehyde were dissolved in 50 cc. absolutely dry acetone, and cooled down to 0° at least. Further, 2.5 grams of sodium were dissolved in 50 cc. absolutely anhydrous alcohol, and also cooled down to 0°. Finally, 10 grams tartaric acid were dissolved in 50 cc. water. Then a solution of sodium ethylate was added to the solution of the aldehyde in acetone, the whole being kept cooled and continually stirred, and in fifteen minutes the reaction was interrupted by the addition of the solution of tartaric acid. Now the acetone and alcohol were distilled with water vapor; the residual oil was separated from the solution of tartaric acid and washed. The oil thus obtained after one distillation with superheated steam was rectified either under diminished pressure or purified by means of a solution of sodium bisulphite. For this purpose 50-gram portions of the crude acetone condensation-product were boiled with 100 cc. commercial solution of sodium bisulphite, and 100 cc. water, for about three hours in a vessel connected with an inverted condenser. After the whole was cooled down the small quantities of substances which were not ketones were carefully removed by extracting with ether, and the bisulphite double compound decomposed in the cold with caustic soda. The separated oil was well washed and rectified, first with superheated steam and then under diminished pressure. The analyses and physical constants of the three aldehyde and acetone condensation-products are given in the table farther on.

<sup>1</sup> German patent No. 73089.

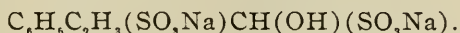


The ketones obtained in this way were then characterized by means of their semicarbazones, which were prepared exactly in accordance with the directions given above, with this difference, that they were finally recrystallized, not from methyl alcohol and water, but from a good deal of ligroin boiling at  $105^{\circ}$ – $140^{\circ}$ . The melting-points of the semicarbazones are also given in the table.

It is evident from the above table that by means of sodium bisulphite, three aldehydes,  $C_{10}H_{16}O$ , can be obtained from oil of lemon-grass, which differ distinctly from one another. The condensation-products with acetone also show marked differences, and all can be transformed into different ring-compounds which are ketones having the odor of violets, but none of them gives irone. The geranylidene-acetone gives Tiemann's ionone, while the citriodorylidene-acetone and the allo-lemonyldene-acetone give new ketones with the odor of violet, which form the "artificial oil of violets" of Franz Fritzsche & Co. Besides the naphthocinchonic acids and the different condensation-products with acetone, the conduct of their compounds with sodium bisulphite is especially characteristic for the three aldehydes themselves.

Citriodoric aldehyde easily forms a very solid compound with bisulphite if not too great an excess of the sodium bisulphite is taken, and the proportion of aldehyde to 35 per cent. sodium bisulphite to water is as 1 : 2 : 2. This solid compound, after standing for a short time, dissolves, forming a clear solution, heat being evolved, and from this the aldehyde can be separated only by means of caustic soda or by boiling with sodium carbonate.

Cinnamic aldehyde,  $C_6H_5.CH : CH.CHO$ , conducts itself in a similar way. Fr. Heusler<sup>1</sup> has found that it passes into solution in the form of the compound



All aldehydes that contain the group  $X-CH : CH.CHO$  seem to have the power to form bisulphite compounds of this kind, and, therefore, considering the relation of citriodoric

<sup>1</sup> Ber. d. chem. Ges., 24, 1805.

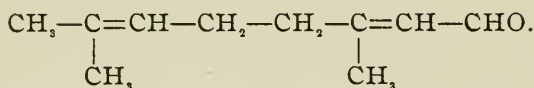
Table Giving the Properties of the Aldehydes ( $C_{10}H_{16}O$ ) from Oil of Lemon-Grass, and of their Derivatives

Name.....	Citridioric aldehyde. Dodge: This JOURNAL, 12, 553.	Citral—Geranial. Tiemann and Semmler: Ber. d. chem. Ges., 26, 2709; 31, 820.	Allo-lemonal-Laevo- licarhodol Barbier: Compt. rend., 122, 84.
Literature .....			
B. p. under 12 mm.	108°-109°	111°-112°	117.5°-119°
B. p. " 760 mm.	228°-229°	225°-227°	233°-235°
Sp. gr. at 20°	0.8883	0.8868	0.9017
Refraction $n_D$ at 20°	1.48538	1.48752	1.48306
Rotation for 1 dm $\alpha_D$ at 20°	$\pm 0^\circ$	$\pm 0^\circ$	$-5^\circ 5'$
M. R. for $C_{10}H_{16}O$ (47.53)	49.07	49.34	48.15
Calc. for $C_{10}H_{16}O$ : C = 78.95 p. c.	78.85	79.20	78.77, 79.00
" " H = 10.53 p. c.	10.95	10.89	11.05, 10.92
M. p. of semicarbazone	134°	141°	169°
$\alpha$ -Semicarbazone }	were not	160° (scales)	could not be
$\beta$ -Semicarbazone }	separated	150° (needles)	separated
M. p. of naphthocin. acid	204°	197°	235°
Calc. for $C_{23}H_{33}NO_2$ : C = 80.00 p. c.	80.00	79.60, 80.20	.....
" " H = 6.67 p. c.	7.10	7.10, 6.90	.....
" " N = 4.06 p. c.	4.10	4.10, 4.10	.....
Conduct of the bisulphite compound when heated }	Dissolves to a clear liquid, and is sepa- rated by NaOH.	Dissolves to a clear liquid, and is not separated by NaOH.	All allo-lemonal sepa- rates. It is easily re- duced to the alcohol.

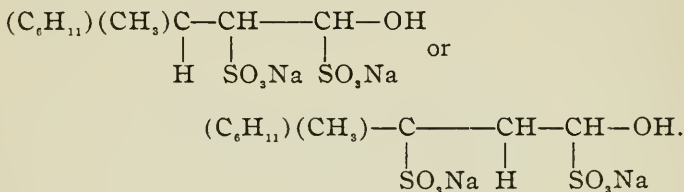
## Acetone Condensation-products of the Above Aldehydes.

Name .....	Citriodoric aldehyde. Dodge: This JOURNAL, 12, 553.	Citral—Geranial. Tiemann and Semmler: Ber. d. chem. Ges., 26, 2709; 31, 820.	Allo-lemonal-Laevo- licarhodol. Barbier: Compt. rend., 122, 84.
B. p. under 12 mm.	149°-152°	143°-145°	157°-159°
Sp. gr. at 20°	0.8980	0.9037	0.9000
Refraction $n_D$ at 20°	1.52903	1.52736	1.5315
M. R. for $C_{13}H_{20}O$ , 60.94	65.94	65.35	66.05
Calc. for $C_{13}H_{20}O$ : C = 81.25 p. c.	81.12	81.17	81.0
“ “ “ H = 10.42 p. c.	10.70	10.77	10.38
M. p. of semicarbazone	134°-135°	110°-112°	142°-143°
Obtained from oil of lemon-grass	40-50 per cent. Citriodoric aldehyde	8-10 per cent. Citral-Geranial	25-30 per cent. Allo-lemonal

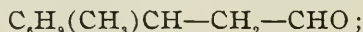
aldehyde to the ketones of the violets (see below), it probably has the following constitutional formula :



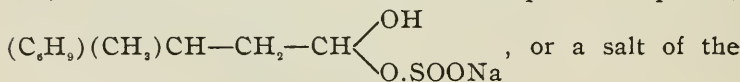
For the easily soluble double compound with bisulphite, the following two formulas are worthy of consideration :



Geranial (citral) conducts itself in an entirely different way. This compound is formed in considerable quantity from natural oil of lemon-grass under the influence of strongly acid, freshly prepared sodium bisulphite, as has already been indicated and as will be proved further on; and when geranial (citral) is treated with the same bisulphite in the same proportion, 1 : 2 : 2, a beautiful solid bisulphite compound is also obtained, and this under ordinary circumstances crystallizes in good form after standing for twenty-four hours. If this compound is heated in the liquid in which it is formed, it is partly dissolved and crystallizes out on cooling. If, however, the heating is continued long enough a clear solution is also obtained from which neither sodium carbonate nor caustic soda regenerates an oil either at ordinary temperature or when boiled. According to Tiemann and Semmler,<sup>1</sup> the sodium salt of a true sulphonic acid is formed. In other respects, however, the bisulphite compound of geranial conducts itself perfectly normally, so that it does not contain the end group X—CH : CH.CHO, but must have the formula,



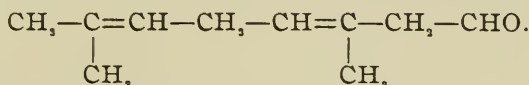
and, therefore, forms the normal bisulphite compound,



<sup>1</sup> Ber. d. chem. Ges., 26, 2710.

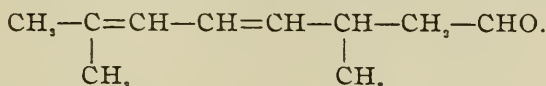
sulphonic acid,  $(C_6H_9)(CH_3)CH-CH_2-CH \begin{cases} OH \\ SO_2OH \end{cases}$ .

According to its relations to the ionone<sup>1</sup> which has been well investigated, it probably has the following constitutional formula :



Finally, allo-lemonal conducts itself toward sodium bisulphite quite normally, but it differs, nevertheless, essentially from geranial in this respect : Its compound with sodium bisulphite is decomposed at a comparatively low temperature and thus easily regenerates the allo-lemonal. If, therefore, allo-lemonal is shaken with bisulphite and water in the proportion 1 : 2 : 2, a solid bisulphite compound is obtained in a short time, and this when heated yields allo-lemonal again, and does not form a sulphonic acid. While citriodoric aldehyde can be heated repeatedly for any length of time with sodium bisulphite without undergoing a material change, and can be separated afterwards by means of caustic soda ; and while geranial, on the other hand, disappears entirely under these circumstances, allo-lemonal, if heated long enough, is reduced by the hot solution of bisulphite to the corresponding alcohol (allo-lemonol). It appears, therefore, on account of its normal conduct towards sodium bisulphite, that allo-lemonal must also have the formula,  $(C_6H_9)(CH_3)CH-CH_2-CHO$ .

Further, on account of its optical activity, allo-lemonal must also contain an asymmetric carbon atom. On account of its relations to the ketones of violets, which will be made clear below, it must have the following constitutional formula :



The existence of three aldehydes,  $C_{10}H_{16}O$ , in oil of lemon-grass is therefore proved with certainty. These are Dodge's

<sup>1</sup> Compare F. Tiemann's formula for ionone, Ber. d. chem. Ges., 31, 857, 864, 867, 870, 874.

citriodoric aldehyde, the geranial (citril) of Tiemann and Semmler, and Barbier's laevo-licarhodol or allo-lemonal. Certain phenomena which have presented themselves in the course of my investigations, especially the rise of the boiling-point of the mixture of aldehydes above the boiling-point of allo-lemonal, and the existence of a substance which is markedly laevo-rotatory, boiling at a high temperature and having the odor of cedar wood, caused me to suspect that at least a fourth optically active unknown aldehyde of another constitution is contained in oil of lemon-grass; and for this reason I shall continue this investigation in the direction indicated.

### III. *Transformations of the Three Aldehydes of Oil of Lemon-grass into One Another.*

If in the preparation of geranial (citril) from the oil of lemon-grass, a large excess of strongly acid freshly prepared sodium bisulphite is used, materially more geranial is obtained than when the commercial solution of the bisulphite is used in the proportion 1 : 2 : 2. If the assumption is made (an assumption which I have shown to be unfounded) that natural oil of lemon-grass contains geranial, and an attempt is made to increase the yield of aldehyde by oxidation of the oil with potassium bichromate and sulphuric acid, it will be found that by means of sodium bisulphite as well as by means of condensation with acetone, much more geranial or pseudo-ionone is obtained than otherwise. From the oil of lemon-grass which is transformed under the circumstances mentioned, the  $\alpha$ -geranyl- $\beta$ -naphthocinchonic acid melting at  $197^{\circ}$  is obtained. This is scarcely formed at all under ordinary circumstances.

Barbier and Bouveault<sup>1</sup> first called attention to the fact that the other aldehydes  $C_{10}H_{16}O$  are transformed into the most stable one, geranial, by means of acetic or dilute sulphuric acid (or in general by acid agents, even sodium bisulphite). These transformations are similar to those of linalool, licareol, licarhodol into geraniol. I have found, further, that apparently no geranial at all appears to be contained in the oil of lemon-grass, and that this is formed by the transformation of

<sup>1</sup> Compt. rend., 122, 84-86.



the citriodoric aldehyde and allo-lemonal, as pure oil of lemon-grass which has not been brought in contact with acids gives no pseudoionone nor ionone, as I have often shown experimentally.

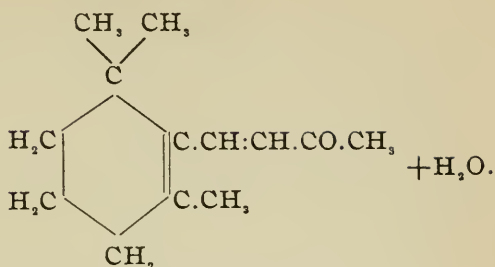
If, however, the oil of lemon-grass is previously treated with sulphuric acid, abundant quantities of pseudoionone and ionone are obtained in consequence of condensation or rearrangement.

It follows from this that only geranial (cital) or oil of lemon-grass that has been completely transformed by means of sulphuric acid, bisulphite, etc., can yield pseudoionone and ionone, while natural oil of lemon-grass can give only citriodorylidene and allo-lemonyldiene-acetone whose cyclic ketones form the "artificial oil of violets" of Franz Fritzsche & Company. But I have observed also another kind of transformation of the three aldehydes: If perfectly pure geranial<sup>1</sup> is boiled with a 20 per cent. solution of sodium acetate for some hours, an oil is obtained that boils at 108°–119°, and the lowest fraction of this oil conducts itself like citriodoric aldehyde. The middle fraction is unchanged geranial, and the highest one conducts itself like allo-lemonal towards sodium bisulphite, as well as in regard to the melting-point of its naphthocinchoninic acid. The sodium acetate under these circumstances seems to act as a very weak alkaline reagent, and it appears that under certain conditions more strongly alkaline agents and the carbonates of the alkalis first effect a similar transformation before they act further upon the aldehydes.

In natural oil of lemon-grass, therefore, only citriodoric aldehyde and allo-lemonal are contained, because in the condensation with acetone with the aid of sodium alcoholate, only citriodorylidene- and allo-lemonyldiene-acetone are obtained, and because, according to this method, as is also noted by F. Tiemann, "other chemical changes need not be feared," as this condensation takes place at very low temperature, in a

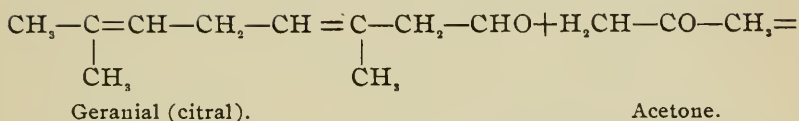
<sup>1</sup> Boiling at 111–112° under 12 mm. pressure forming a naphthocinchoninic acid melting at 197°, and conducting itself towards bisulphite in a manner characteristic of geranial.



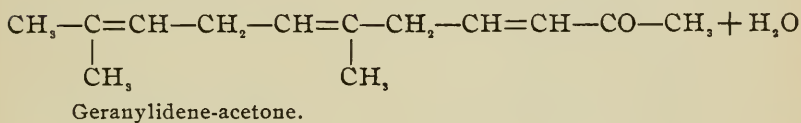


Cyclo-citriodorylidene-acetone.

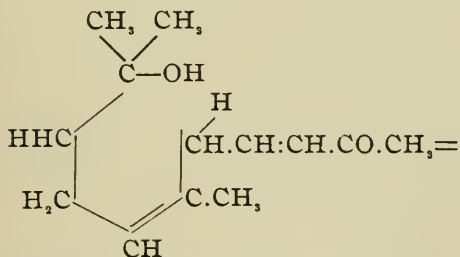
B. *Geranial* (Citrals).



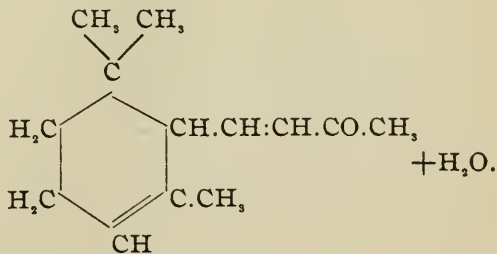
### Acetone.



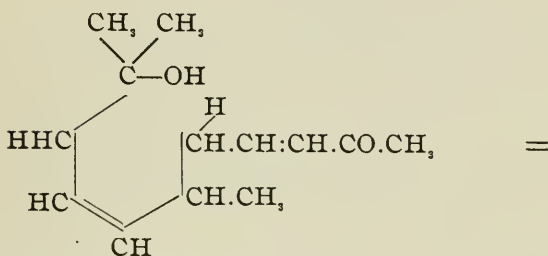
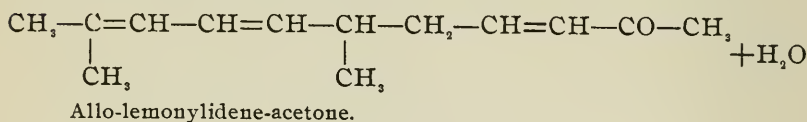
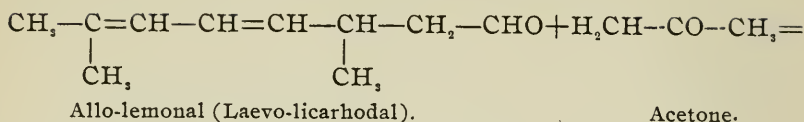
Geranylidene-acetone.



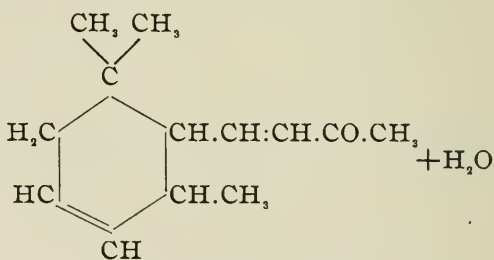
Hydro-geranylidene-acetone.



Gyclo-geranylidene-acetone.

C. *Allo-lemonal* (*Laevo-licarhodal*).

Hydro-allo-lemonylidene-acetone.



Cyclo-allo-lemonylidene-acetone.

Upon the basis of his extensive investigations of irone and ionone,<sup>1</sup> F. Tiemann reaches the conclusion that the existence of four structurally isomeric substances can be foreseen, and that all of these may be expected to have the odor of violets. Three of these four formulas of violet ketones are identical with those which I have presented above.

The cyclo-citriodorylidene-acetone is identical with Tiemann's second hypothetical violet ketone.

<sup>1</sup> Ber. d. chem. Ges., 31, 867.

The cyclo-geranylidene-acetone is Tiemann's ionone.

The cyclo-allo-lemonyldiene is Tiemann's first hypothetical violet ketone.

The fourth violet ketone is natural irone, the synthesis of which has not thus far been effected.

I intend later to publish a more complete investigation of these violet ketones, the formation of which, from the three aldehydes described by me, takes place very simply, and thus furnishes the confirmation of F. Tiemann's theory of the existence of four violet ketones of definite constitution.

The present investigation further places in a clear light the very complicated relations presented in the last publications of F. Tiemann, and his coworkers on the subject of ionone. In his first classical treatise on the aroma of violets,<sup>1</sup> as well as in his patents,<sup>2</sup> and also in the communication on methods of detecting ionone and irone,<sup>3</sup> Tiemann has given the properties of ionone and pseudoionone and their reactions with great accuracy, and he has also stated that these substances were prepared from pure materials (geranial-acetone),<sup>4</sup> and had been obtained in chemically pure condition.

As F. Tiemann<sup>5</sup> in one of his last publications says that citral (geranial) is, up to the present, the only aliphatic terpene aldehyde of the formula  $C_{10}H_{16}O$ , the presence of which has been established in ethereal oils, and thus shows that he does not recognize the existence of citriodoric aldehyde and allo-lemonal, it appears that he has of late used fractionated oil of lemon-grass for the preparation of his ionone, and I have already shown that this consists principally of citriodoric aldehyde and some allo-lemonal, for only in this way is it possible to explain why the pseudoionone and ionone which at first were so sharply characterized, have become so changeable in their constants and reactions.<sup>6</sup>

With the aid of this assumption, it is also possible to see why he now obtains from the ionone a whole series of different

<sup>1</sup> Ber. d. chem. Ges., **26**, 2692.

<sup>2</sup> German Patent No. 73089.

<sup>3</sup> Ber. d. chem. Ges., **28**, 1754.

<sup>4</sup> *Ibid.*, **26**, 2692.

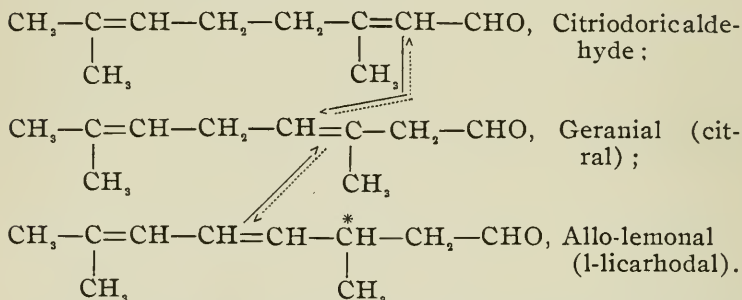
<sup>5</sup> *Ibid.*, **31**, 822.

<sup>6</sup> Compare *Ibid.*, **26**, 2692, with *Ibid.*, **31**, 842, 851, 879.

semicarbazones, for ionone<sup>1</sup> is nothing but the cyclo-allo-lemonylidene-acetone described above, while besides the true ionone the cyclo-citriodrylidene-acetone must also be contained in these products.

It follows from this that Tiemann's ionone can be prepared only from pure geranial, or from sufficiently transformed oil of lemon-grass (cital), while the natural oil of lemon-grass, as well as the separate aldehydes, citriodoric aldehyde and allo-lemonal, must always give the ketones of the "artificial oil of violets" of Messrs. Franz Fritzsche & Co.

In conclusion I give the three constitutional formulas for the aldehydes as they have been deduced from their chemical conduct and from their relations to the violet ketones, and at the same time their transformations are indicated :



The arrows show the passage from citriodoric aldehyde and allo-lemonal to geranial under the influence of acid reagents. The arrows drawn in broken lines show the passage from geranial to citriodoric aldehyde and allo-lemonal under the influence of alkaline reagents. The star indicates the asymmetric carbon atom in allo-lemonal.

In these transformations there occurs only a change of position of one double bond in the aldehydes, either to or from the position of equilibrium in geranial.

This memoir will appear in full in the "Journal für praktische Chemie."<sup>2</sup>

HAMBURG, Aug. 1, 1898.

<sup>1</sup> Ber. d. chem. Ges., 31, 867-881.

<sup>2</sup> See J. prakt. Chem., N. F 58, 51.



## REVIEWS.

### THE FREEZING-POINT, BOILING-POINT, AND CONDUCTIVITY METHODS.

By HARRY C. JONES, Instructor in Physical Chemistry in Johns Hopkins University. Easton, Pa.: The Chemical Publishing Co. 1897. 64 pp. 75 cents.

This little book is a laboratory guide and presents the necessary details for making determinations of molecular weights by the new methods, and for studying the conductivity of solutions, while, at the same time, the theory of the subject is not forgotten. It will no doubt be found useful wherever the methods it treats of are taught—that is to say, in all chemical laboratories where physical chemistry is recognized as an important and necessary part of chemistry.

In describing the boiling-point method, the author confines himself largely to a form of apparatus devised by himself, upon the basis of one previously described by Hite. This gives his work a somewhat one-sided air, but, after all, it was not his purpose to describe all methods in detail, but rather to lay stress upon what appeared to him the simplest and best. His apparatus is simpler and cheaper than that of Beckmann, and, to say the least, gives as good results. Apparently it gives better results.

COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicine, with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S. Past President Society of Public Analysts, Public Analyst for the West Riding of Yorkshire and the City of Sheffield, and the Boroughs of Chesterfield, Doncaster, Rotenham, etc. Third Edition, Illustrated with Revisions and Addenda by the Author, and by HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Metallurgy in the Pennsylvania College of Dental Surgery, and in the Wagner Free Institute of Science, Philadelphia, etc.—VOLUME I.—*Introduction, Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch and its Isomers, Vegetable Acids, etc.* Philadelphia: P. Blakiston's Son & Co. 1898. 557 pp. Price \$4.50.

Allen's "Organic Analysis" consists of four volumes. Two editions of each of the first three volumes have been published, and now, simultaneously, the third edition of Volume I, and the second edition of Volume IV are brought out. A notice of the latter will appear in this Journal later. The author has had all he could attend to in preparing the second edition of his book, which is only just finished. Meanwhile the second edition of the earlier volumes has been exhausted, and

some of the volumes are out of print. Taking advantage of the fact just mentioned a publisher has reprinted Volume I, without consulting the Author. In order now that the publisher may be punished, as he certainly deserves to be, the Author has secured the cooperation of Dr. Henry Leffmann, in the preparation of the needed third edition. A copy of an affidavit is sent out with Volume I, from which the following passage is taken: "The earlier volumes of the above work being out of print he (the author) has authorized Messrs. P. Blakiston's Son & Co. to reprint these earlier volumes with such additions and corrections as they may think proper." He further says "that to facilitate this he has supplied Dr. Henry Leffmann, of Philadelphia, with numerous and valuable addenda with full discretion to use these as he may think fit; that the work as thus revised is the only issue authorized by him in any way in the United States of America, that he has carefully examined the reprint of Volume I of 'Commercial Organic Analysis' recently issued, and finds that it misrepresents his present views in regard to a large number of matters, even the errata which were discovered after the publication of Volume I, and lists of which were published in the later volumes, remaining uncorrected in this reprint; that he protests strongly against the issue of this unauthorized and uncorrected reprint of a book fourteen years old, which issue has been effected without his knowledge or concurrence, and that Messrs. P. Blakiston's Son & Co. are his authorized agents and publishers in the United States of America."

The facts stated in this affidavit should be known to every chemist, but especially to those who have bought or are intending to buy the book.

Allen's "Organic Analysis" is so well known that it is unnecessary to review the new volume in detail. Those who are engaged in analytical work cannot do without it. It is such a book as can be written only by a chemist who has had extensive experience in dealing with practical chemical problems, and one who is also a careful student and investigator.

This volume, as the title-page informs us, deals with "alcohols, neutral alcoholic derivatives, sugars, starch and its isomers, vegetable acids, etc." "The neutral alcoholic derivatives" treated of are ether, compound ethers (esters), aldehydes, chloral, chloroform. Under "alcohols" methods for the analysis of wine, cider, malt liquors, spirits, liqueurs or cordials, and tinctures are given. There are many inter-

esting revelations regarding adulterations. Thus, on page 161 occurs this statement: "The green color of absinthe ought to be due to chlorophyll, introduced from spinach nettles, or parsley. A mixture of sulphate of indigo with picric acid or turmeric is not unfrequently employed, and salts of copper have also been used." Among the substances liable to be found in bread are "magnesium carbonate, alum and equivalent preparations containing aluminium, plaster of Paris, whiting, and barium sulphate (page 449). On page 453 it is stated that "*Sulphate of Copper* was formerly employed as an adulterant of bread, especially in foreign countries, and a recent instance of its employment in this country has been recorded." In regard to honey we are told (page 381) that it "is frequently adulterated, the most common sophistication being the addition of glucose syrup, a dextrinosaccharine liquid obtained by the action of dilute acid on starch. A factitious honey is sometimes manufactured wholly from glucose syrup, with addition of minute quantities of formic acid, and flavors to give the preparation the flavor of honey."

While these and many other similar statements are interesting reading, it must be said that, for the most part, the adulterating substances are used in such minute quantities as to be of no importance from the sanitary point of view.

A few slips have been noted. On page 37, Frauenhofer is spelled "Frauenhöfer"; and on page 257 "Schiebler" occurs instead of Scheibler. Under chloroform (page 232), the author states that this substance is prepared from alcohol and from chloralhydrate. In a foot-note he says; "Acetone \* \* may be substituted for alcohol in the preparation of chloroform." The reader would get the impression that acetone is used, if used at all, only to a slight extent; whereas, as a matter of fact, in Germany and in this country at least, very large quantities of chloroform are manufactured from acetone.

According to the classification now adopted by chemists the polyatomic alcohols, such as mannite and dulcite, are not called sugars. The author says (page 243): "Glycerol and glycol have a sweet taste, and, like the sugars, are polyatomic alcohols;" and, also: "Most of the sugars have the constitution of hexatomic alcohols, or of aldehydes or ethers derived therefrom. True mannite, which is  $\alpha$ -hexone alcohol,  $C_6H_8(OH)_6$ , by limited oxidation with platinum-black yields the corresponding aldehyde,  $C_6H_8(OH)_6$ , which is a true sugar called mannitose." Of course, the formula given for mannitose is wrong. It should be,  $C_6H_8(OH)_6CHO$ . The "American Academy of Sciences," referred to on page 369, should be "The National Academy of Sciences."

Most of the slips noticed are, however, of little importance. The book is excellent, as all chemists know, and it will continue to be the standard in the subject with which it deals.

I. R.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS. BY E. F. LADD, B.S., Professor of Chemistry in the North Dakota Agricultural College, and Chemist to the Government Experiment Station, Fargo, N. D. New York: John Wiley & Sons. 82 pp. 1898.

The author has prepared this book for beginners, and has selected methods which he says are not always the ones which will give the most reliable results, but are such as will aid in developing the reasoning powers of the student. The explanation of details has been omitted as the student is expected to refer to larger works for these facts. The book contains, besides general directions, methods for gravimetric and volumetric analyses of metals, acids, etc., and methods used in the analysis of ashes, soils, ores, food-stuffs, water, and urine. The student could not get a clear idea of the chemical principles involved from the very condensed form of the directions as given here, and it would perhaps be more satisfactory if the part relating to such subjects as water and urine analyses was omitted, and the general principles explained more fully, as such works as those of Fresenius and Crookes are not always available and are themselves very mechanical. These difficulties can, however, be overcome by a competent instructor, and under such a director the book would perhaps prove as successful as it has in the hands of the author.

J. E. G.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. By HENRY W. SCHIMPF, Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy. Third Edition. New York: John Wiley & Sons. 1898. pp. xxix, 522.

It is one of the unfortunate evils of our educational system that a text-book should have to be written for a particular class of students instead of dealing with a subject in a manner broad enough to be suitable for all classes. In his preface the author, states that the book "is designed for the use of pharmacists, and especially as a text-book for students in pharmacy." This is more or less of an admission that there is either something wrong with the subject, or with the students, and we are inclined to believe that it is the poor preliminary training of the students. The pharmacist—and the book will be useful only to pharmacists—after he has done most of the experiments will not have obtained a clear, general idea of volumetric analysis, but will have received a



certain mechanical training in the determination of certain substances. The U. S. Pharmacopoeia has been taken as the basis of the book, and this is mostly responsible for the manner of treating the subject. The author has accepted the conditions as they have existed for a number of years without trying to improve upon the method of presenting the subject.

The book is divided into four parts treating of: I. "A Systematic Arrangement of Volumetric Processes" including pharmaceutical methods for inorganic substances. II. The Volumetric Analysis of Various Medicinal Acids and Salts. III. Sanitary Analysis. IV. Gasometric Analysis.

The first part treats of general principles, apparatus, standard and normal solutions, indicators, and calculations and then proceeds to the preparation of standard solutions. For each solution prepared the author gives the reaction taking place, neutralization or precipitation as the case may be, and directly under the equation gives the molecular weight of each substance and shows the number of grams to the litre for the reactive reagent; thus on pages 64-68, the reaction of sulphuric acid with eight separate carbonates is written out, and as many times the student is shown that there are 49 grams of  $H_2SO_4$  entering the reaction. On pages 115-128 we see at least sixteen times the reaction of silver nitrate on chlorides, iodides and bromides, with molecular weights and almost as many examples of calculations. This endless repetition of reactions, with their corresponding figures, is not confined to any one class of reactions but is general throughout the book. There are extremely few generalizations, the subject matter is not logically developed, and there is no attempt made to show the reliability or accuracy of the various methods. Much space is consumed by repetitions of a process for different salts of the same acid as in the case of hypophosphorous acid on pages 163-169, where the reactions and process are repeated for the calcium, iron, potassium and sodium salts, when one statement of the reaction of all would have been sufficient.

Part III, treating of the sanitary analysis of water, milk, butter, soap, wine, and analysis of drugs and alkaloids is free from most of the objections raised against the rest of the book.

The illustrations, with few exceptions, show forms of apparatus which for the most part are never used, such as the various obsolete forms of burettes.

H. F.

A MANUAL OF CHEMICAL ANALYSIS, QUALITATIVE AND QUANTITATIVE.  
By G. S. NEWTH, F.I.C., F.C.S. New York & London: Longmans,  
Green & Co. 1898.

In this book of 462 closely printed pages, the first 186 pages

are given to qualitative analysis, 106 to gravimetric, 114 to volumetric methods, and 30 to analysis of organic compounds and physical chemical determinations. An appendix contains useful tables. The book is good, and sufficiently thorough for college and technical students. It is well illustrated with plates of apparatus and manipulation. It is scarcely necessary to say to those familiar with the author's excellent book on "Lecture-room Experiments" that the methods are good and that they are clearly described. Prof. Newth's book is recommended to those who desire a book covering the entire field.

E. R.

AN INTRODUCTION TO THE SCIENCE AND PRACTICE OF QUALITATIVE CHEMICAL ANALYSIS, INORGANIC. By CHAPMAN JONES, F.I.C., F.C.S. London & New York: Macmillan & Co. 213 pp. \$1.50.

Still another manual of analysis combining to some extent a text-book of chemistry with an analytical manual by including part, but not all of the average text-book information. The book is clearly written has the 'table' system in pronounced degree, is as good as most other manuals of the same type but offers nothing new.

E. R.

CHEMICAL AND METALLURGICAL HANDBOOK, containing Tables, Formulas, and Information for the use of Chemists, Metallurgists, and Mining Engineers. By J. H. CREMER, M.E., and G. A. BICKNELL, M.S. Second Edition. Cleveland, Ohio. 1898.

This little book is something on the order of the German Chemiker-Kalender, though it does not contain as much. The Table of Molecular Weights, Specific Gravities, Melting-points, Boiling-points, and Solubilities of the Principal Inorganic Compounds (pages 24-54) is highly suggestive of Biedermann's book. There are tables of all sorts presented. Among them the following may be specially mentioned: Analytical reactions, specific gravity of alcohol, sulphuric acid, hydrochloric acid, nitric acid, of ammonia and the caustic alkalies, methods for analysis of iron ore, pig iron, steel, coal and coke, minerals, methods used in assaying, logarithms, etc., etc. The book appears to be worthy of commendation.

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*Correction.*

✓ Vol. 19, page 404, line 15: For "114°" read "119°-120°."



# AMERICAN CHEMICAL JOURNAL

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Contributions from the Kent Chemical Laboratory of the University of Chicago.

## ON THE CONSTITUTION OF THE SALTS OF IMIDO- ETHERS AND OTHER CARBIMIDE DERIVATIVES.

BY JULIUS STIEGLITZ.

Substances containing a carbimide group ( $C=NR$ ) are usually found to unite readily with acids, especially with hydrochloric acid. The addition-products in nearly every case have the appearance of salts, and in most cases their properties. From the first discovery of these compounds the tendency has been to ascribe the formation of such salts to the presence of the nitrogen atom alone, the addition-products being considered derivatives of ammonium salts  $C=N^+RHC\ell$  simply because they are salts. In one or two cases it has already been shown that the hydrogen chloride is really taken up at the double bond of the carbimide group or by the carbon atom alone. Thus, the addition-products of the isocyanates,  $OC:NR$ , and hydrogen chloride, the urea chlorides, have been shown by Gattermann<sup>1</sup> to be chlorformamides,  $ClCONHR$ . The addition-products of hydrocyanic acid,  $C:NH$ , and fulminic acid,  $C:NOH$ , with hydrogen chloride have in general the constitution of acid imide chlorides, *e. g.*,  $ClCH(:NOH)$ ,<sup>2</sup> the chlorine atom going to the carbon. These very hydrochlorides, however, for which the ammonium form of constitu-

<sup>1</sup> Ann. Chem. (Liebig), **244**, 29.

<sup>2</sup> Nef: *Ibid.*, **287**, 342, etc.; **280**, 303.

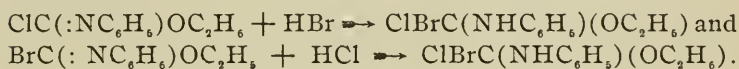
tion has been rejected are not salts of bases but are rather acid chlorides. In the case of the salts of true carbimide bases like the imido-ethers,  $\text{RC}(:\text{NR})\text{OR}$ , the amidines,  $\text{RC}(:\text{NR})\text{NHR}$ , the pyridines, quinolines, etc., it has been assumed without further experimental evidence that they must be ammonium salts with quinquivalent nitrogen  $[\text{C}(:\text{N}^{\text{V}}\text{RHCl})]$ . The alternative constitution  $[\text{CCl}(\text{NHR})]$ , has not been considered for such derivatives, probably for the reason that the grouping  $\text{C}-\text{Cl}$  has always been held to be necessarily either an *acid chloride* grouping as in  $\text{RCOCl}$ ,  $\text{RC}(\text{NR})\text{Cl}$ , etc., or a hydrochloride acid *ester* grouping as in the alkyl chlorides. In terms of the theory of ionization chemists have accepted the positive ammonium ions  $\text{R}_4\text{N}^+$ , whose existence is beyond any doubt, but the possibility of the existence of positive carbon ions  $\text{R}_3\text{C}^+$  has as yet hardly been considered or, when considered, rejected off-hand.<sup>1</sup> The very fact of ionization of chlorides has been used to disprove the possibility of chlorine being attached to carbon.<sup>1</sup> It is true the behavior of simple carbon derivatives undoubtedly containing the group  $\text{C}-\text{Cl}$ , the alkyl halides, etc., so far as studied, seems entirely in accord with such a course, although minimal ionization into  $\text{R}_3\text{C}^+$  and  $\text{Cl}^-$  in such cases has not been disproved, and even seems probable.<sup>2</sup> But should this not prove to be the case, it would not dispose of the possibility that under certain favorable conditions we can have positive carbon ions, salts of carbon bases which are capable of stronger electrolytic dissociation. We have sulphur, phosphorus, iodine bases, etc., why not carbon bases? It has been chiefly with the object of getting further experimental evidence on this subject, either for or against the possibility suggested, that a series of studies has been undertaken and partly completed in the last two years by my students in this laboratory. A favorable starting-point seemed to be the carbimide bases mentioned above. The behavior of the hydrochlorides of imido-ethers, particularly the ease with which they break down at comparatively low temperatures into alkyl chloride and acid amide led me to suspect that they

<sup>1</sup> Miolati: Ber. d. chem. Ges., **26**, 1788; **28**, 1696; Tortelli: *Ibid*, **28**, 1702.

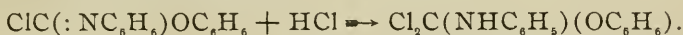
<sup>2</sup> *Vide e. g.*, Ostwald: Lehrb. allgem. Chem., Vol. II, 788.

really have the constitution  $\text{RC} \begin{array}{l} \diagup \text{NH}_2 \\ \text{--- Cl} \\ \diagdown \text{OC}_2\text{H}_5 \end{array}$ . Facts observed in

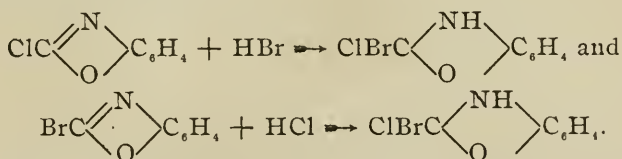
the course of an investigation in collaboration with Dr. Lengfeld on the action of phosphorus pentachloride on urethanes<sup>1</sup> led us to the same conclusion, and induced us to test it by comparing the hydrobromide of chlorformphenylimido-ether with the hydrochloride of bromformphenylimido-ether.<sup>2</sup> The results pointed to the formation of the same salts in both cases thus :



This salt could not be isolated on account of its extreme instability. It decomposed even at  $-15^\circ$ . But from the fact that the same decomposition-products (chiefly ethyl bromide and chlorformanilide) were obtained in both reactions, the intermediate formation of the same addition-product was inferred. That such a salt is capable of existence under more favorable conditions of the molecule was demonstrated by the preparation and analysis of the hydrochloride of chlorformphenylimidophenyl ester :



The subject seemed, however, too important to rely entirely on the formation of an intermediate product which was not isolated in the critical test. For this reason, Mr. H. N. McCoy at my request has tested the question further by comparing the hydrobromide of chlorformphenyleneimido-ether with the hydrochloride of bromformphenyleneimido-ether. As described in Mr. McCoy's paper (see next article) these salts were *isolated* and proved *identical*. They must therefore be formed according to :



<sup>1</sup> Lengfeld and Stieglitz : This JOURNAL, 16, 76.

<sup>2</sup> This JOURNAL, 17, 93.

That such addition-products are true salts of bases, however weak the bases are, was proved by their solubility in water in presence of an excess of acid, and by the preparation and analysis of a chlorplatinate and a nitrate corresponding to the hydrochloride of chlorformphenyleneimido-ether. Therefore, unless rearrangements in the molecule, extremely improbable under the conditions of the experiments, have taken place, the constitution of the salts of these imido-ethers is that of carbon bases and not of ammonium bases. These facts, in connection with the results of Dr. Lengfeld and myself, and the analogous behavior of all imido-ethers, warrant the conclusion that the salts of all imido-ethers have the constitution  $RCX(NHR)(OR)$ . This conclusion is being still further tested<sup>1</sup> in as many different ways as seem possible. So far all direct experimental evidence points one way.

In another case the possibility of the existence of salts of carbon bases of the nature indicated has been investigated. According to Mr. McCoy's results (see next article) which confirm the preliminary conclusions of Lengfeld and myself,<sup>2</sup> the constitution of the hydrochloride of carbodiphenylimide,  $C(:NC_6H_5)_2$ , is expressed by the formula  $(C_6H_5NH)(C_6H_5N:)CCl$ . And Mr. F. B. Dains<sup>3</sup> working under my direction in this laboratory has shown that the salt-forming power of carbodiphenylimide is not confined to hydrochloric acid. He has prepared and analyzed a number of chlorplatينات of carbodialphylimides, whose composition,  $[(RNH)(RN:)C]_2PtCl_6$ , corresponds to that of their chlorides. Undoubtedly the chlorides have also some resemblance to acid chlorides, being rapidly decomposed by water and reacting readily with sodium alcoholate, but the dual character

<sup>1</sup> One method is indicated in a preliminary report by Mr. Ransom (Ber. d. chem. Ges., 31, 1055), who will report later in this JOURNAL. Another method that Mr. Wm. McCracken will use is the attempt to prepare two isomeric dichlorides

$C_6H_4 \begin{array}{c} \diagup O \\ \diagdown NCH_3 \end{array} CCl_2$  and  $C_6H_4 \begin{array}{c} \diagup O \\ \diagdown N \\ \diagup CH_3 \\ \diagdown Cl \end{array} CCl$  and study the salt characteristics of a body of

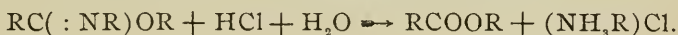
the former constitution.

<sup>2</sup> This JOURNAL, 17, 107; Stieglitz: Ber. d. chem. Ges., 28, 573.

<sup>3</sup> Vide a paper by Mr. Dains which will appear in one of the next numbers of the Journal of the American Chemical Society.

repeats only in an organic compound what is quite common in inorganic chlorides.<sup>1</sup>

Mr. Dains<sup>2</sup> has also made an exhaustive study of the chemical behavior of the aromatic isourea ethers, for instance ethylisocarbanilide,<sup>3</sup>  $(C_6H_5NH)(C_6H_5N:)COC_2H_5$ . His work has led to very interesting and instructive results bearing both on the constitution of the salts of imido ethers and on their general chemical behavior. Ethyl isocarbanilide, although it contains both the basic phenylimido-ether group  $-C(:NC_6H_5)(OC_2H_5)$  and the second basic anilido group  $C_6H_5NH-$  is a *mono-acid* base. It unites with 1 molecule of hydrochloric acid giving  $(C_6H_5NH)C(:NC_6H_5)(OC_2H_5) \cdot HCl$ , and its chlorplatinate has the composition  $[(C_6H_5NH)C(:NC_6H_5)OC_2H_5]_2H_2PtCl_6$ . This agrees best with the constitution  $(C_6H_5NH)_2CCl(OC_2H_5)$  for the hydrochloride. This view of the constitution is strongly supported by the behavior of the urea ether towards aqueous hydrochloric acid. The ordinary imido-ethers heretofore known, such as ethyl imido-benzoate, ethyl phenylimidoformate, etc., show a reaction which has been considered typical for the imido-ethers: with dilute aqueous acids they are rapidly saponified even in the cold into amines and acid esters according to:



Alkyl isocarbanilides are very much more stable; they are not decomposed completely even after standing weeks in cold dilute acids, and when they are decomposed by dilute hydrochloric acid, they invariably react as follows:



yielding ethyl chloride and a carbanilide, and not aniline and a urethane! Considering that such a striking change of reaction takes place in going simply from weaker bases to much stronger ones of the same class of compounds, and that the

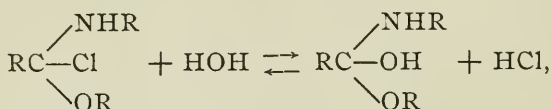
<sup>1</sup> An interesting reaction of acetic acid on carbodiallylimides, investigated by Mr. Dains, supports the constitution given above to the hydrochloride of carbodiallylimide; the evidence will be fully discussed by Mr. Dains in his paper in the *Journal of the American Chemical Society*. Compounds  $(R_2N)(RN:)CCl$  will also be prepared to obtain further light on the question.

<sup>2</sup> *Loc. cit.*

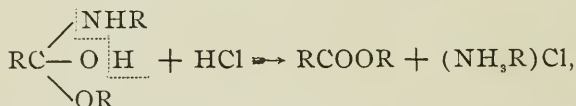
<sup>3</sup> Lengfeld and Stieglitz: *Ber. d. chem. Ges.*, **27**, 926; *This JOURNAL*, **17**, 984; and Stieglitz: *Ber. d. chem. Ges.*, **28**, 573.



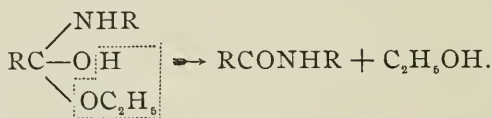
difference in behavior is only shown towards aqueous acid—all of the compounds belonging to the class of imido-ethers give alkyl chlorides and acid amides with anhydrous hydrogen chloride—the conclusion is inevitable that the change in behavior must be due to the different hydrolytic action of water on the chlorides. As among inorganic chlorides we have gradual changes in action towards water on going, *e. g.*, from phosphorus pentachloride through aluminium and magnesium chloride to sodium chloride, there can be no doubt that the hydrochlorides of imido-ethers with weaker basic functions must be hydrolyzed more or less in aqueous solution, and that the stronger the basicity of the imido-ether the smaller the degree of hydrolysis of the chloride. Ordinary imido-ethers like benzimidoethyl ether, formphenylimidoethyl ether, etc., being much weaker bases than the urea ethers, their hydrochlorides must be more or less hydrolyzed in aqueous solution:<sup>1</sup>



and the free imido ether base formed can readily break down into an amine and an acid ester according to



or, under certain conditions, into alcohol and an acid amide:<sup>2</sup>



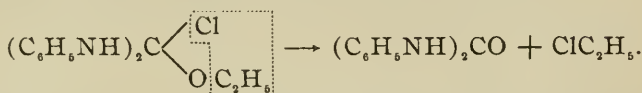
The urea ethers being much stronger bases, their hydrochlorides are found to be much more stable in aqueous solution,

<sup>1</sup> The hydrochloride of benzimidoethyl ether that had stood for a number of months over solid potassic hydrate in a desiccator gave a solution in water which immediately reacted decidedly acid towards litmus. A solution of the hydrochloride of metanitrobenzimidoethyl ether showed a very strong acid reaction.

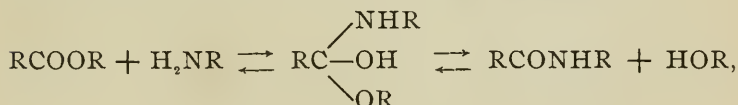
<sup>2</sup> Comstock and Wheeler: This JOURNAL, 13, 522.



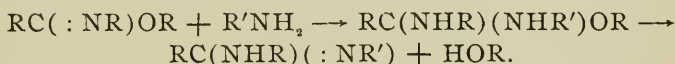
and, when they do decompose, they slowly give the decomposition-products of the hydrochlorides themselves :



No other conception of the constitution of the hydrochlorides of imido-ethers and urea ethers explains so simply their different behavior towards aqueous acids.<sup>1</sup> This interpretation of the constitution of the hydrochlorides of the isocarbanilides is further supported by another important discovery concerning the chemical behavior of the isocarbanilides. A second reaction of the imido-ethers, which hitherto had to be regarded as typical is that with amines, yielding amidines with great ease. In the analogous action of amines on acid esters it is now commonly assumed that the reaction takes place with the formation of an intermediate product<sup>2</sup> as follows :



and there is every reason to suppose that in the action of amines on imido ethers the same kind of intermediate addition product is formed :<sup>3</sup>

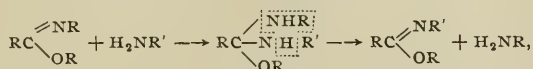


It is worth noting that the imido-ethers react the more rapidly and easily in this direction, the more negative their molecule

<sup>1</sup> The characteristic difference between the imido-ethers and the urea ethers recalls the fact that amidines like *s*-benzodiphenylamidine,  $\text{C}_6\text{H}_5\text{C}(:\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$ , are much more readily saponified to anilines and benzanilides than the corresponding guanidines are (Wallach : Ann. Chem. (Liebig), 184, 85); *e. g.*, triphenylguanidine,  $(\text{C}_6\text{H}_5\text{NH})\text{C}(:\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$ . The explanation given for the former case fits admirably the amidines as well.

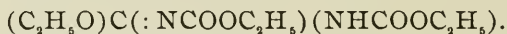
<sup>2</sup> *Vide, e. g.*, Lossen : Ann. Chem. (Liebig), 252, 193.

<sup>3</sup> This is made practically certain by the fact that besides an amidine very frequently a new imido-ether is formed according to :



(Lossen : Ann. Chem. (Liebig), 265, 138).

is. Thus phenylimidoformic ethers,<sup>1</sup> succinimido-ether,<sup>2</sup> etc., give amidines especially readily. Naturally, the addition of the positive amine groups is facilitated by the negative condition of the amido-ether. Now, where the imido-ether is very strongly positive, as is ethyl isocarbanilide, this typical imido-ether reaction is almost entirely suppressed. Under all ordinary conditions aniline and ammonia do not react at all with ethyl isocarbanilide; only by prolonged heating with aniline at 200° in a sealed tube was a small amount of triphenylguanidine obtained.<sup>3</sup> It seems plausible that such a positive urea ether should take up and hold hydrochloric acid so firmly as described above and that it should resist the addition of aniline at the same place in the molecule, an addition which, as shown, seems necessary to make it react at all with aniline. In this way we have the same simple cause for both the abnormal (new) characteristics of the isocarbanilides in which they differ so strikingly from ordinary imidoethers. The intimate connection of the two was shown by Mr. Dains by preparing a urea ether with more negative radicals, ethyl isodicarbethoxylurea,



This compound is rapidly decomposed by hydrochloric acid and it also reacts readily with ammonia, forming dicarbethoxylguanidine  $(\text{NH}_2)\text{C}(:\text{NCOOC}_2\text{H}_5)(\text{NHCOOC}_2\text{H}_5)$ .

Further evidence on the constitution of the hydrochloride of ethyl isocarbanilide can be drawn from its behavior towards benzoyl chloride. This is fully discussed by Mr. Dains in his paper on the subject.

All the experimental data gathered in this laboratory on the subject of the constitution of the hydrochlorides of imidoethers and similar carbimide bases point, therefore, in the same direction, that these salts are not ammonium salts but are formed by the addition of hydrogen chloride to the double bond of the carbimide group,  $\text{C}:\text{NR}$ . A glance at the literature brings strong indications confirming such a view, not only for imidoethers but closely allied imido derivatives. It

<sup>1</sup> Comstock and Kleeberg : *This JOURNAL*, **12**, 498.

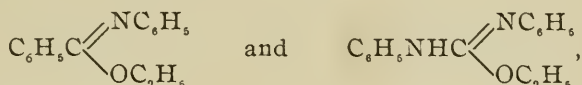
<sup>2</sup> Comstock and Wheeler : *Loc. cit.*

<sup>3</sup> Dains : *Loc. cit.*

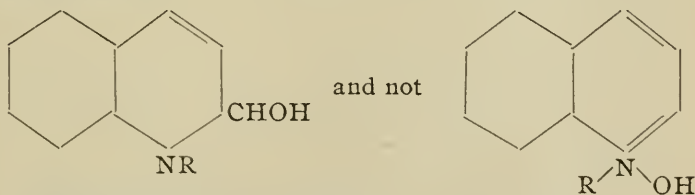
is a significant fact that phenylimidobenzoic ether, *s*-diphenylbenzamidine, and triphenylguanidine,



all form salts with one molecule of acid in spite of the increasing number of amine groups. They all have one double bond ( $\text{C}:\text{NC}_6\text{H}_5$ ) in common—nothing else. In the same way phenylimidobenzoic ether and ethyl isocarbanilide (anilidophenylimidoformic ether),



form salts with only one molecule of acid. On the other hand, carbodiphenylimide, carboditolylimide, etc.,  $\text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5$ , etc., with two double bonds, take up two molecules of hydrogen chloride<sup>1</sup> with such avidity that it was a matter of greatest experimental difficulty to isolate a monochloride;<sup>1</sup> and carbanilide  $(\text{C}_6\text{H}_5\text{NH})_2\text{CO}$ , with no carbimide double bond but two anilido groups does not form any hydrochloride! These facts so strongly corroborate direct experimental evidence discovered so far, that the work will be continued along analogous lines on the constitution of the salts of the amidines, thioimido-ethers, etc., as well as the imido-ethers. It will include an investigation of the constitution of the salts of pyridine and quinoline. The hydroxides obtained from alkylquinolinium salts are now considered, according to the investigations of Roser,<sup>2</sup> Decker,<sup>3</sup> etc., to have the constitution

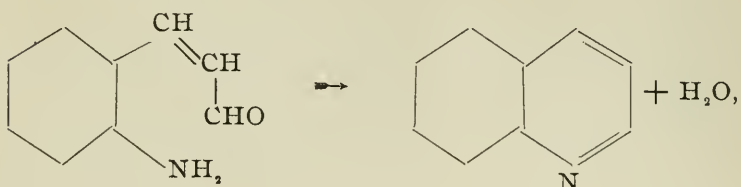


<sup>1</sup> Lengfeld and Stieglitz: This JOURNAL, 17, 107; Dains: *Loc. cit.*

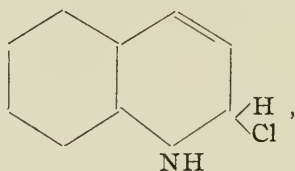
<sup>2</sup> Ann. Chem. (Liebig), 272, 221; 282, 373.

<sup>3</sup> Ber. d. chem. Ges., 25, 3326; J. prakt. Chem., 45, 161; 47, 222.

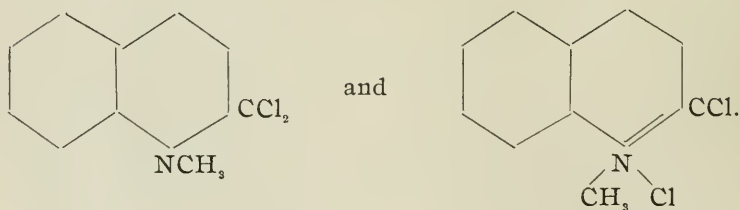
an ammonium hydroxide. The salts, however, are still universally supposed to be ammonium salts, even by Roser and Decker, while no experimental evidence has been brought to bear on the subject. Quinoline is a phenylimide derivative (phenyleneimidoacrolein) as is shown by its synthesis (from *o*-amidocinnamic aldehyde)



and constitution, and it seems possible that its salts should have the constitution



corresponding to that developed for phenylimido-esters, and to that of the hydroxides obtained from the quinoline salts. The problem of the constitution of the pyridine and quinoline salts will be investigated in the near future, by comparing the hydrochloride of  $\alpha$ -bromquinoline and the hydrobromide of  $\alpha$ -chlorquinoline as well as by an attempt to prepare isomeric dichlorides,



The work completed and outlined deals entirely with the constitution of salts of carb(phenyl)imide derivatives. The foothold obtained in working on the imido-ethers and carbodi-phenylimide seems to indicate that accumulation of positive imido groups attached to a carbon atom transfers their positive effect to make the carbon radical a positive ion. It may be added that on account of the importance of the question of the existence of carbon ions  $R_3C^+$  and, in view of the behavior of ordinary compounds containing the group  $C-Cl$ , a great deal of hesitation is felt in accepting any results as final before more evidence is collected; but, so far, the experimental results have been surprisingly unanimous in support of the views expressed. Should they continue to be so, the ultimate aim will be to find carbon bases free from nitrogen, and it is hoped that such will be found in some tertiary alcohols.

CHICAGO, October, 1898.

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## ON THE HYDROCHLORIDES OF CARBO-PHENYL- IMIDO DERIVATIVES.

HERBERT N. MCCOY.

Many bodies containing the carbo-phenylimido group,  $C=NC_6H_5$ , combine readily with acids, particularly the halogen acids, to form salt-like compounds. In the preceding paper by Prof. Stieglitz, it is shown that it is a question of considerable importance to determine experimentally whether, in any given class of such compounds, the acid is taken up by the nitrogen atom, forming ammonium derivatives; or is absorbed by the double bond between carbon and nitrogen, the halogen going to the carbon and the hydrogen to the nitrogen atoms, while the valence of the nitrogen remains unchanged.

The work, an account of which is given in the present paper, was undertaken at the suggestion and under the direction of Dr. Stieglitz, with the object of investigating two such cases. The first part of the paper deals with the experiments on the constitution of the hydrochlorides, etc., of phenylimido acid esters,  $RC(:NR)OR$ ; the second part comprises a study

of the constitution of the addition-products of hydrogen chloride and carbodiphenylimide,  $C(:NC_6H_5)_2$ .

## PART I.

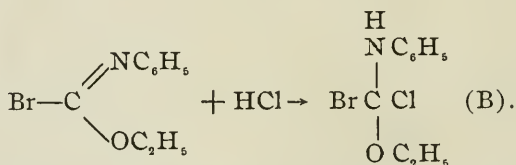
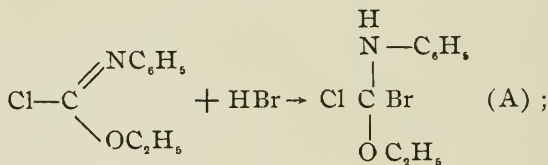
*On the Hydrochlorides of Phenylimido Acid Esters.*

The imido esters,  $R''C(:NR)OR'$ , form crystalline salts with acids<sup>1</sup>, particularly with the halogen acids. These salts have been considered by their discoverer, Pinner, and by others, to have the general constitution, (I)  $R''C(OR')(:N^VRHX)$ , the nitrogen atom being quinquivalent.

In 1894 Lengfeld and Stieglitz<sup>2</sup> in the course of a study of the action of phosphorus pentachloride on phenylurethane, were led to examine the question whether the salts of the imido esters might not have the constitution represented by

the formula, (II)  $R''C \begin{array}{l} \text{H} \\ \diagup \\ \text{NR} \\ \diagdown \\ \text{X} \\ \diagup \\ \text{OR}' \end{array}$ , the hydrogen haloid having been

added to the double bond. The results of their investigation of the action of hydrogen bromide on ethyl phenylimidochlorformate and of hydrogen chloride on ethyl phenylimidobromformate indicated that in both cases the same addition-product or salt is formed. This is only possible if formula II represents the true constitution of these salts.



The products A and B should be identical. The identity

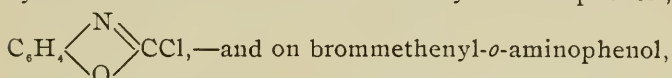
<sup>1</sup> Pinner : Ber. d. chem. Ges., 10, 11, 16, 17, etc.

<sup>2</sup> This JOURNAL; 16, 70; 17, 98.



of these salts could not be proved by isolating them, as they decompose below  $-15^{\circ}$ . However, as A and B gave the same *decomposition-products* (in both cases chiefly ethyl bromide and chlorformanilide) the only simple explanation is to be found in the assumption that the above identical addition-compounds are the intermediate products of the reaction.

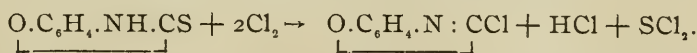
The fact that the salts mentioned were too unstable to be isolated and compared directly made it desirable to obtain and compare more stable salts of the same class of compounds. With this object in view, I have investigated the salts formed by the action of acids on chlormethenyl-*o*-aminophenol<sup>1</sup>,



$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CBr}$ , compounds which are imido-esters of the same type as the compound  $\text{R}''\text{C}(:\text{NC}_6\text{H}_5)\text{OR}$ .

A great deal of work was necessary in order to find suitable methods for preparing the substances.

Chlormethenylaminophenol (carbonylaminophenol chloride) had been prepared by Seidel<sup>2</sup> by the action of phosphorus pentachloride on *o*-thiocarbamidophenol; but the yield was poor, and the method failed entirely, in attempting to prepare the brommethenylaminophenol, necessary for the investigation, by the action of phosphorus pentabromide on the thio-compound. After trying a number of methods described below, it was found that these two substances can be prepared very readily and with excellent yields by the action of dry chlorine or bromine on the thio-compound suspended in dry chloroform, and subsequent treatment with water, thus :



On account of the ring structure of these imido esters the hydrogen-haloid addition-products should show no tendency to split off aliphyl haloid, corresponding to a loss of ethyl haloid in the case of the bodies studied by Lengfeld and Stieglitz;

<sup>1</sup> Concerning the nomenclature *vide* Ladenburg : Ber. d. chem. Ges., 10, 1124.

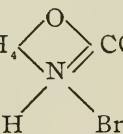
<sup>2</sup> J. prakt. Chem., [2], 42, 454.

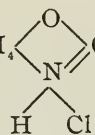
in fact, the addition-products were found to be capable of isolation.

The hydrochloride, obtained by the action of dry hydrogen chloride on a ligroin solution of chlormethenylaminophenol is a white crystalline salt-like body, which is stable in an atmosphere of hydrogen chloride at the ordinary temperature, and decomposes, with loss of hydrogen chloride, at  $57^{\circ}$ . Water dissociates the salt at once into hydrochloric acid and chlormethenylaminophenol; but in concentrated hydrochloric acid chlormethenylaminophenol, which is an oil insoluble in water, is very readily soluble and separates as the unchanged oil, on diluting with water; thus showing that the oil is a true, though weak base.

The hydrobromide of chlormethenylaminophenol, obtained by the action of carefully dried hydrogen bromide on a solution of the chlorine compound in dry ligroin, was found to be a fairly stable substance, decomposing, when dry, only above  $155^{\circ}$ .

The hydrochloride of the corresponding brommethenylaminophenol, prepared from the latter by the addition of dry hydrogen chloride, had the same composition, melting-point and other properties as the above hydrobromide of chlormethenylaminophenol. The salts are decomposed by water, *both giving hydrobromic acid and chlormethenylaminophenol*. The two bodies appear to be identical in every respect. This can only be the case when both bodies are represented by the formula,  $\text{O}-\text{C}_6\text{H}_4-\text{NH}-\text{CClBr}$ ; while according to the old concep-

tion the bodies would have the formulas,  $\text{C}_6\text{H}_4$    $\text{CCl}$  and

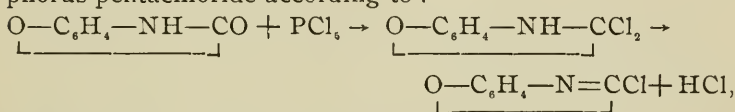
$\text{C}_6\text{H}_4$    $\text{CBr}$ , and they would evidently have different prop-

erties. Besides those mentioned, other salts of these substances were prepared and analyzed: the nitrate, and the

chlorplatinate of chlormethenylaminophenol, and the hydrobromide of brommethenylaminophenol, thus establishing their salt-like nature beyond a doubt.

The results of the investigation of the salts of chlor- and of brommethenylaminophenol are therefore in complete accord with the views of Lengfeld and Stieglitz<sup>1</sup> on the constitution of the salts of the amido ethers. Carbo-phenylamido derivatives are weak bases and the hydrogen-haloid addition-products are true salts, in which *the halogen is bound to carbon* and the hydrogen to nitrogen; and they may in general be represented by the formula,  $R''C \begin{matrix} \text{NHR} \\ \text{---X.} \\ \text{OR'} \end{matrix}$ .

In connection with the investigation of the salts of chlormethenylaminophenol, the opportunity was used to study the action of phosphorus pentachloride on carbonylaminophenol somewhat more fully than had been done by previous investigators.<sup>2</sup> It was decided to determine whether carbonylaminophenol or certain of its derivatives would react with phosphorus pentachloride according to :



with the object, not only of finding a convenient method for preparing the halogen methenylaminophenols used in this work; but more particularly of getting more evidence on the action of phosphorus pentachloride on urethanes, which action was supposed to take place according to the equation just given.<sup>3</sup> The results obtained were in accord with those of Bender and of Chelmiki. Chlormethenylaminophenols could in no case be obtained (except perhaps in traces) by the action of phosphorus pentachloride on any of the derivatives of carbonylaminophenols. While, as a method of preparation, the experiments have proved unsuccessful, they show, in connection with the results of Bender and Chelmiki, that the action of phosphorus pentachloride on urethanes does not take place according to the above equation.

<sup>1</sup> *Loc. cit.*, and Stieglitz : This JOURNAL, 21, 101.

<sup>2</sup> Bender : Ber. d. chem. Ges., 19, 2271; Chelmiki : *Ibid.*, 20, 178.

<sup>3</sup> Lengfeld and Stieglitz : This JOURNAL, 16, 72.

## EXPERIMENTAL PART.

*The Action of Potassium Hypobromite on Salicylic Amide.*

In order to prepare the carbonylaminophenol needed, a new method was tried, starting from salicylic amide, and based on the molecular rearrangement which bromamides show when treated with alkalies or alcoholic sodium methylate<sup>1</sup>.

The preparation of salicylic amide by heating the methyl ester with concentrated aqueous ammonia<sup>2</sup> gives good results only when the heating is continued several days at 100°. By heating, in a sealed tube, one part of the ester with two parts of 36 per cent. ammonia and one and one-half parts of pure methyl alcohol for six hours at 100°, very good yields of the amide were obtained. The alcohol greatly accelerates the action by dissolving both the ester and the ammonia. From theoretical considerations, it is evident that the ultimate yield of amide must be somewhat diminished by the use of alcohol; but the cheapness of the material, the greater purity of the product, and the saving of time make the new method preferable.

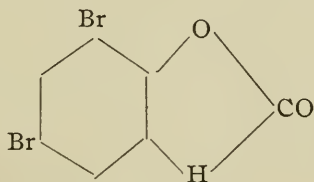
To prepare salicylic bromamide the method of Hoogewerff and Van Dorp<sup>3</sup> was adopted. To an alkaline solution of potassium hypobromite, made from one molecule of bromine and four molecules of caustic potash in 10 per cent. solution, was added one molecule (5 grams) of dry salicylic amide in small portions, the temperature of the solution being kept below 5°. The amide dissolved forming a clear solution, which, treated with cold dilute acetic acid, gave a nearly white precipitate. This was not the expected salicylic bromamide, since, when treated with potassium iodide and hydrochloric acid, no iodine was liberated. Further examination showed the precipitate to consist of a body containing bromine mixed with much unchanged salicylic amide. A second experiment, with two molecules of bromine and six of caustic potash to one of the amide, gave a similar product which, however, contained less unchanged amide. Finally, one molecule of salicylic amide

<sup>1</sup> Hofmann; Ber. d. chem. Ges., **15**, 762; Hoogewerff and Van Dorp: Recueil trav. chim., **9**, 33; **10**, 4; Lengfeld and Stieglitz: This JOURNAL, **15**, 215, 504; **16**, 370.

<sup>2</sup> Spilker: Ber. d. chem. Ges., **22**, 2768.

<sup>3</sup> Rec. trav. Chim., **4**, 373.

(5 grams) was added to the alkaline hypobromite solution, obtained from three molecules of bromine (17.8 grams) and eight molecules of caustic potash (16.5 grams) in 150 cc. of water. This reaction like the two preceding was carried out below 5°. The nearly white precipitate, obtained with cold dilute acetic acid, did not react with potassium iodide; thus showing the absence of bromamide. From hot glacial acetic acid the body crystallizes on cooling in spherical aggregates of almost colorless needles melting at 243°–247°. Very slight decomposition seems to take place on boiling with acetic acid. After several recrystallizations from benzene, in which the body is but slightly soluble, the substance is pure white, and melts at 250°. The new body was proved to be 3-5-dibromcarbonylaminophenol,



by its analysis, by its reduction to carbonylaminophenol, and by its synthesis from 3-5-dibromsalicylic amide.

0.3790 gram gave 17.5 cc. N<sub>2</sub> at 23.5° and 738.6 mm.

	Calculated for C <sub>7</sub> H <sub>3</sub> Br <sub>2</sub> NO <sub>2</sub> .	Found.
N	4.79	5.07

Jakoby<sup>1</sup> has made a dibromcarbonylaminophenol (m. p. 243°–245°), by the action of bromine water on a water solution of carbonylaminophenol. When a sample of the substance, prepared according to Jakoby, was compared with the above substance the two were found to have quite similar properties, but that they were not identical was shown by the melting-point (about 210°) of a mixture of the two; each substance, separately, melts 35–40° higher. The reduction of both of the above bodies to carbonylaminophenol is readily accomplished.

<sup>1</sup> J. prakt. Chem., [2] 37, 51.



*Reduction of Dibromcarbonylaminophenol.*—0.2 gram of Jakob's dibrom body was shaken thirty minutes with 10 grams of  $2\frac{1}{2}$  per cent. sodium amalgam and 25 cc. of water; the body, being readily soluble in alkali, soon dissolved. After filtering from mercury and acidifying, the white precipitate formed was crystallized from hot water. It formed colorless needles, free from bromine, melting at  $138^{\circ}$ , and having all the properties of carbonylaminophenol; by mixing with pure carbonylaminophenol, the melting-point remained unchanged.

One gram of the dibrom body from salicylic amide was reduced by sodium amalgam as above. The precipitate with acid was free from bromine; from hot water it crystallized in colorless needles, which melt at  $138^{\circ}$ . The properties of the substance are those of carbonylaminophenol; its complete identity with this body was established by the melting-point,  $138^{\circ}$ , of their mixture. The last experiment furnishes conclusive proof that the dibrom body obtained by the action of hypobromite on salicylic amide is a dibrom derivative of carbonylaminophenol.

The isomerism of the body obtained from salicylic amide, with that obtained by brominating carbonylaminophenol directly, pointed to a bromination of the aromatic ring as the first step of the reaction of hypobromite on salicylic amide.

*Synthesis of 3-5-Dibromcarbonylaminophenol.* — Salicylic amide reacts with aqueous bromine with the greatest ease, forming 3-5-dibromsalicylic amide.<sup>1</sup> To a solution of 10 grams of 3-5-dibromsalicylic amide, made according to Spilker, and 4 grams (2 molecules) of caustic potash in 180 cc. of water, cooled to  $0^{\circ}$ , was added slowly an ice-cold solution of hypobromite resulting from 5.4 grams (1 molecule) of bromine and 5 grams ( $2\frac{1}{2}$  molecules) of caustic potash in 60 cc. of water. A white crystalline mass resulted. The crystals, which were evidently the potassium salt<sup>2</sup> of the dibromcarbonylaminophenol, were filtered from a slightly colored mother-liquor; dissolved in 250 cc. of water, and an excess of dilute acetic acid added. The white amorphous precipitate formed was filtered off; washed with water, in which it is

<sup>1</sup> Spilker; Ber. d. chem. Ges., 22, 2769.    <sup>2</sup> Vide, p. 119.

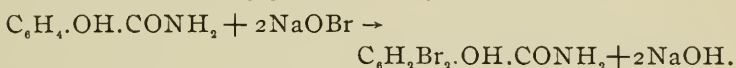


nearly insoluble ; and dried on a clay plate. The yield was 6.7 grams. After recrystallization from hot benzene the substance was perfectly pure. It had the melting-point,  $250^{\circ}$ , and all the properties of the body obtained by the action of 3 molecules of hypobromite on salicylic amide ; by mixing with the latter, the melting-point remained unchanged. A bromine determination confirmed the identity.

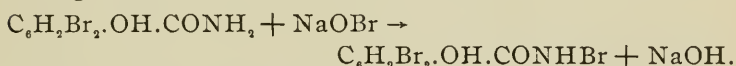
0.1303 gram heated with lime gave 0.1674 gram AgBr.

	Calculated for $C_7H_5Br_2NO_2$ .	Found.
Br	54.61	54.80

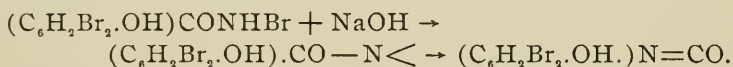
The first product of the action of hypobromite on salicylic amide is, therefore, 3-5-dibromsalicylic amide :



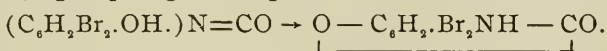
This, by the action of another molecule of hypobromite, must give 3-5-dibromsalicylic bromamide :



The bromamide undergoes rearrangement so rapidly that it at once gives the isocyanate <sup>1</sup>:



The latter reacts immediately with the neighboring phenol-hydroxyl group to give the product obtained :



The great ease with which dibromsalicylic bromamide is rearranged is remarkable. In no other case has such a rearrangement taken place so rapidly, that the bromamide could not be isolated.

Aside from the ease with which the process takes place, the whole series of reactions is perfectly normal.

*Salts of Dibromcarbonylaminophenols.*—Both dibromcarbonylaminophenols form salts with alkalis. The potassium salt of Jakoby's body was obtained as well-formed white

<sup>1</sup> Stieglitz : This JOURNAL, 18, 75.

needles, by the addition of an excess of 30 per cent. caustic potash to a clear solution of the dibrom body dissolved in a little dilute solution of caustic potash. The salt was purified by dissolving it in acetone, in which it is readily soluble, and adding ligroin (boiling-point  $60^{\circ}$ – $70^{\circ}$ ), when the salt separated in beautiful white needles, which decompose above  $300^{\circ}$ . The analysis was made by dissolving the salt in water, adding  $\frac{N}{10}$ -hydrochloric acid in slight excess, and titrating back with  $\frac{N}{10}$ -potassium hydroxide using methyl orange. The dibrom body was precipitated by the acid, but was not filtered off, as it does not affect the indicator.

0.4739 gram required 14.6 cc.  $\frac{N}{10}$ -HCl; calculated for  $C_7H_2Br_2NO_2K$ , 14.3 cc.

The sodium salt, white needles, was prepared similarly.

0.7525 gram required 24.2 cc.  $\frac{N}{10}$ -HCl; calculated for  $C_7H_2Br_2NO_2Na$ , 23.9 cc.

The salts of 3-5-dibromcarbonylaminophenol resemble the above salts, but are more soluble in water and acetone.

*The Action of Phosphorus Pentachloride on Dibromcarbonylaminophenol.*—Attempts<sup>1</sup> to obtain chlormethenylaminophenol by the action of phosphorus pentachloride on carbonylaminophenol have led to a mixture of bodies chlorinated in the ring. The action of phosphorus pentachloride on Jakoby's dibromcarbonylaminophenol was tried with the hope that, owing to the protection afforded by the halogen already in the ring, a chlormethenyldibromaminophenol would result, by a smooth reaction. It was found that phosphorus pentachloride does not act on the dibrom body when the two are heated with dry, boiling chloroform, in which the dibrom body is somewhat soluble; neither do the dry substances react when heated all day in a sealed tube at  $100^{\circ}$ . At  $200^{\circ}$  a reaction took place; the tube contained hydrochloric acid, and the black residue had the odor of phosphorus oxychloride. About one-third of the material used was recovered unchanged, but no other pure substance could be isolated.

<sup>1</sup> Bender: Ber. d. chem. Ges., 19, 2271; Chelmiki: *Ibid.*, 20, 178.

*The Action of Phosphorus Pentachloride on the Sodium Salt of Carbonylaminophenol.*

Carbonylaminophenol was prepared according to Bender's<sup>1</sup> method, from his so-called ethyl aminophenylcarbonate,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OCOOC}_2\text{H}_5$ . The latter was made from ethyl *o*-nitrophenylcarbonate. Instead of using an alcoholic solution of potassium nitrophenol, I treated the aqueous solution of the potassium salt with chlorcarbonic ether and obtained quantitative yields of ethyl nitrophenylcarbonate, which I found distills with no apparent decomposition at  $176^\circ-178^\circ$  under 21 mm. pressure. It was found too that alcohol could be omitted with advantage, in the reduction which is readily accomplished when concentrated hydrochloric acid is added in small portions to a mixture of tin and the ester, the flask being cooled to prevent much rise of temperature. After diluting the solution of the reduced substance with an equal volume of water, and filtering from the remaining tin and sediment, a perfectly clear and colorless solution is obtained. This solution may be kept several hours without showing signs of crystallization, but slowly deposits pure white crystals on prolonged standing. If, however, the clear solution is heated to  $90^\circ$  for 10 minutes, it becomes very turbid with oily drops, and on cooling the whole of the reduction product separates *at once* in the form of white crystals. The latter are now insoluble in dilute acids, but dissolve readily in alkalies. In spite of the fact that the body is an *acid* and *not a base*, Bender described it as aminophenylethyl carbonate,  $\text{NH}_2-\text{C}_6\text{H}_4-\text{OCOOC}_2\text{H}_5$ , which no doubt exists at first in the acid solution obtained in the reduction. Mr. J. H. Ransom<sup>2</sup> working in this laboratory, on this subject with Dr. Stieglitz has now proved that a rearrangement takes place in the acid solution leading to the formation of oxyphenylurethane,  $\text{C}_2\text{H}_5\text{O}_2\text{CNHC}_6\text{H}_4\text{OH}$  or  $\text{NH}-\text{C}_6\text{H}_4-\text{O}-\text{C}(\text{OH})\text{OC}_2\text{H}_5$ .

The results of this investigation will be published at a later date in this Journal.

<sup>1</sup> Ber. d. chem. Ges., 19, 2269.

<sup>2</sup> *Ibid.*, 31, 1055.

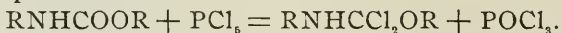
By heating the above urethane to  $230^{\circ}$  it was converted into carbonylaminophenol, with loss of alcohol.

Upon mixing a concentrated solution of carbonylaminophenol in absolute alcohol with the calculated amount of alcoholic sodium ethylate, a gray crystalline precipitate of the sodium salt is formed, the amount of which is increased by the addition of ligroin. The salt is very easily soluble in water and in alcohol; with dilute acids, even carbonic acid, carbonylaminophenol is regenerated.

The dry sodium salt was treated with phosphorus pentachloride, under various conditions, with the hope of obtaining chlormethenylaminophenol. The reaction was always complicated, giving a mixture of products from which very little and often none of the desired body could be isolated. It was thought possible that ethoxymethenylaminophenol,  $\text{O}-\text{C}_6\text{H}_4-\text{N}=\text{C}-\text{OC}_2\text{H}_5$ , might be converted into chlor-

methenylaminophenol by the action of phosphorus pentachloride. This ester has been made from *o*-aminophenol and imido-carbonic ester<sup>1</sup>; but for this experiment it was prepared by the action of alcohol and sodic hydrate on chlormethenylaminophenol, which latter is readily obtained in another way (see below). The body thus made had the boiling-point and other properties ascribed to it by Sandmeyer. By heating with aqueous hydrochloric acid it was readily split into carbonylaminophenol and ethyl chloride. The ester reacts with phosphorus pentachloride only on heating, but no chlormethenylaminophenol was found in the resulting product.

The experiments just described prove that it is impossible to replace the carbonyl oxygen in carbonylaminophenol by halogen by any possible variation of the conditions. They show that it is extremely unlikely, that the action of phosphorus pentachloride on any urethane takes place according to the equation:



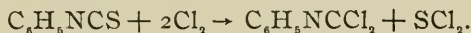
As these methods failed to lead to chlor- and brommethenylaminophenols, I returned to Seidel's method for the preparation of the former body; *viz.*, by the action of phosphorus

<sup>1</sup> Sandmeyer: Ber. d. chem. Ges., 19, 2655.

pentachloride on thiocarbamidophenol. In this reaction, besides the body desired, other products containing chlorine and phosphorus were also obtained, as has already been observed by Seidel. The separation of pure chlormethenylaminophenol from these by-products and the phosphorus sulphochloride formed is very troublesome, and the yield is usually poor; while with phosphorus pentabromide not a trace of the corresponding brommethenylaminophenol was obtained.

The chlorinating effect of phosphorus pentachloride made it seem probable, that, in Seidel's reaction, the formation of chlormethenylaminophenol was chiefly due to the action on the thio body of chlorine, liberated from phosphorus pentachloride at the temperature used. If this were true, by using chlorine alone, under the most favorable conditions, a much smoother reaction should occur.

As a precedent, the case of phenyl mustard-oil may be mentioned; when heated with phosphorus pentachloride<sup>1</sup> this gives a mixture of phenylimidocarbonyl chloride, chlormethenylaminothiophenol and other chlorinated products; while, by the action of chlorine<sup>2</sup> *in the cold*, Nef<sup>3</sup> has obtained only phenylimidocarbonyl chloride, in almost quantitative yield:



The following reaction shows the correctness of the above assumption.

*The Action of Chlorine on o-Thiocarbaminophenol:—Chormethenylaminophenol, O—C<sub>6</sub>H<sub>4</sub>—N=CCl.*

Ten grams of finely powdered and carefully dried *o*-thiocarbaminophenol, made according to Dünner,<sup>4</sup> was suspended in 100 grams of perfectly dry chloroform free from alcohol, in which the thio-body is not very soluble; and carefully dried chlorine slowly passed into the mixture. The flask was cooled with water to prevent a rise of temperature above 20°. The chlorine is readily absorbed at first, and the stream is continued until absorption no longer takes place. The chloroform solution, in which the reaction-products are easily solu-

<sup>1</sup> Hofmann: Ber. d. chem. Ges., 12, 1127.

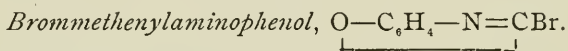
<sup>2</sup> Sell and Zierold: *Ibid.*, 7, 1228.

<sup>3</sup> Ann. Chem. (Liebig), 270, 284.

<sup>4</sup> Ber. d. chem. Ges., 9, 465.

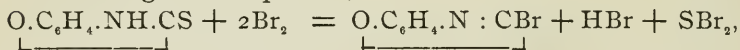


ble, is poured slowly, with vigorous shaking, into half a liter of cold water, in order to decompose the sulphur dichloride formed. After washing with dilute caustic soda and water, until no odor of chlorine or sulphur chloride remained, the chloroform solution was dried with calcium chloride and distilled. 9.2 grams of nearly colorless oil resulted, which, on redistillation gave 8.5 grams of a pure colorless oil, boiling at  $200^{\circ}$ . The substance has the boiling-point, the odor, and other properties of chlormethenylaminophenol, obtained by the action of phosphorus pentachloride on thiocarbaminophenol. With aqueous hydrochloric acid it is readily decomposed, giving carbonylaminophenol (m. p.  $138^{\circ}$ ). Its index of refraction, as determined with the Abbey refractometer, at  $20^{\circ}$ , is 1.5678.



As has already been stated, the action of phosphorus pentabromide on thiocarbaminophenol does not give the above bromide; neither is the chlorine in chlormethenylaminophenol replaced by bromine by treating the chlor body with an excess of bromine. Attempts to prepare the bromide by a method similar to that by which the chloride was obtained (*viz.*, by the direct action of halogen on thiocarbaminophenol) were not at first successful.

According to the equation,



two molecules of bromine are required for each molecule of the thio-body; and this was the amount used in the first experiments which proved unsuccessful. Only when much more bromine (7 to 8 atoms) is used can the bromide be obtained. 38 grams of bromine, in 50 grams of pure *dry* chloroform, were added very slowly, with constant shaking, to 10 grams of thiocarbaminophenol, suspended in 75 grams of pure dry chloroform. At first a heavy brick-red precipitate is formed; but, with an excess of bromine this changes to a heavy, insoluble, dark oil. After adding the bromine, which requires perhaps three-quarters of an hour, the mixture is

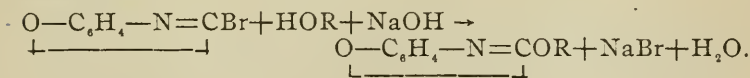


allowed to stand a short time; then treated with water and sodic hydrate, as in the preparation of chlormethenylaminophenol. The treatment with water causes the insoluble oil to become soluble in chloroform; the latter, after drying with calcium chloride, was distilled off, leaving an oily residue. This oily residue, consisting chiefly of brommethenylaminophenol, was treated with ligroin (b. p. 40–60°), which dissolves the brom-body leaving a small, dark residue. Its purification is best accomplished by passing into the ligroin solution pure dry hydrogen bromide, which precipitates the hydrobromide of brommethenylaminophenol. This is filtered off and treated with much water, which causes an immediate decomposition into hydrobromic acid and brommethenylaminophenol; the latter is again taken up in ligroin, and the dried ligroin solution again precipitated with hydrogen bromide. After repeating the precipitation and treatment with water several times, the dried ligroin solution was evaporated in a vacuum, and the last traces of ligroin removed in a current of dry air, in the presence of potassium hydroxide and paraffin. On cooling with ice-water, white crystals were obtained, melting at 27°. These were brommethenylaminophenol as the following analysis shows:

0.2838 gram required 14.2 cc.  $\frac{N}{10}$  AgNO<sub>3</sub>.

	Calculated for C <sub>7</sub> H <sub>5</sub> BrNO.	Found.
Br	40.40	40.03

The analysis was made by treating the substance with alcohol and dilute sodic hydrate, when the following reaction<sup>1</sup> takes place:



The solution was acidulated with nitric acid and titrated according to Volhard.

*Chlormethenylaminophenol Hydrochloride*:—*Dichlorcarbonylaminophenol*,  $\text{O}-\text{C}_6\text{H}_4-\text{NH}-\text{CCl}_2$ .

Carefully dried hydrogen chloride is passed into 0.5 gram of

<sup>1</sup> *Vide*, p. 122.

chlormethenylaminophenol dissolved in 8 cc. of dry low-boiling ligroin, in a well-stoppered vessel, provided with an exit tube. Beautiful white crystals are soon deposited on the walls of the vessel. When the quantity of crystals no longer increases, the liquid is poured off completely and 4-5 cc. of fresh ligroin added, and again decanted. The latter operation is accomplished as quickly as possible to avoid absorption of moisture from the air. The crystals are then freed from ligroin in a current of dry hydrogen chloride, a pump being used to secure a partial vacuum. In a short time the ligroin has evaporated, but a portion of the hydrochloride has decomposed into its constituents. More hydrogen chloride is then passed in until the crystals appear free from oil. The new substance is the very unstable hydrochloride of chlormethenylaminophenol. It is stable only in an atmosphere of dry hydrogen chloride at very nearly atmospheric pressure. It decomposes into its constituents very rapidly in a vacuum, or in dry air, where the partial pressure of hydrogen chloride is also zero. As might be expected it is instantly decomposed by water. A small amount of the hydrochloride, made in a small test-tube, was heated in a water-bath, while a current of dry hydrogen chloride was passed through the tube. Under these conditions the substance melts with decomposition at 57°-58° (thermometer in bath).

The analysis of such an unstable compound cannot, of course, be made by ordinary methods, but was accomplished by quickly bringing the freshly prepared crystals upon a watch-glass, moving this through the air *3 or 4 seconds* to free them from adhering hydrogen chloride, and *immediately* pouring the substance into a tared, wide-mouthed weighing-bottle, containing 25 to 30 cc. of water, and weighing again. The crystals are decomposed at once into hydrochloric acid and chlormethenylaminophenol, which settles to the bottom as a colorless oil. Methyl orange was added and the solution titrated with  $\frac{N}{10}$ -alkali. In neutral or alkaline solution chlormethenylaminophenol is attacked only very slowly by water. In concentrated acid solution, however, it is soluble, and the decomposition by water goes on quite rapidly; but, at the di-

lution used in the analysis, the decomposition is inappreciable.

Substance.	Calculated for $C_7H_5NOCl_2$ (one mol. of acid) cc. tenth-	Found.
Gram.	normal alkali.	cc.
0.1720	9.05	8.65
0.1024	5.39	5.24

Considering the great instability of the body, these figures are as good as could be expected.

*Chlormethenylaminophenol Hydrobromide* :—*Chlorbromcarbonylaminophenol*,  $O-C_6H_4-NH-CClBr$ .

One gram of chlormethenylaminophenol was dissolved in 40 cc. of low-boiling ligroin and treated with dry hydrogen bromide. The hydrobromide of chlormethenylaminophenol appears immediately as a white precipitate, which is much more stable than the hydrochloride. The precipitate was quickly filtered off with a pump, pressed on a clay plate a few moments, and dried in a vacuum over potassium hydroxide for about five minutes. The analysis was made as in the case of the dichloride.

	Substance.	Calculated for $C_7H_5NOClBr$ (one mol. of acid) cc. tenth-	Found.
	Gram.	normal alkali.	cc.
I.	0.3420	14.58	14.35
II.	0.1590	6.78	6.86

The substance is a white powder, which melts at  $155^\circ$  with decomposition. It quickly loses one molecule of acid in contact with water.

The neutralized solution, in analysis II. above, was separated from the insoluble oil and precipitated with silver nitrate. A weighed portion of the dried silver haloid was reduced to metallic silver.

I. 0.1193 gram of the dry silver salt gave 0.0693 gram Ag.

A second preparation of silver haloid was made from the solution resulting from the action of water on another sample of freshly prepared hydrobromide.

II. 0.2220 gram of the dry silver salt gave 0.1304 gram Ag.

	Calculated for AgCl.	Calculated for AgBr.	Found. I.	Found. II.
Halogen	24.73	42.55	41.91	41.26

The result shows that, by the action of water on chlormethenylaminophenol hydrobromide, hydrobromic acid is split off almost without any hydrochloric acid.

*Brommethenylaminophenol Hydrobromide*:—*Dibromcarbonylaminophenol*,  $\text{O}-\text{C}_6\text{H}_4-\text{NH}-\text{CBr}_2$ .  
 $\text{[-----]}$

By passing dry hydrogen bromide into a ligroin solution of brommethenylaminophenol, the hydrobromide is obtained as an almost colorless precipitate. It was dried and analyzed exactly as was the hydrobromide of chlormethenylaminophenol. The new salt melts with decomposition at  $163^\circ$ , and is decomposed by contact with water.

Substance.	Calculated for $\text{C}_7\text{H}_5\text{NOBr}_2$ (one mol. of acid) cc. tenth- normal alkali.	Found.
Gram.		cc.
0.1451	5.20	5.31

*Brommethenylaminophenol Hydrochloride*:—*Chlorbromcarbonylaminophenol*,  $\text{O}-\text{C}_6\text{H}_4-\text{NH}-\text{CBrCl}$ .  
 $\text{[-----]}$

A ligroin solution of brommethenylaminophenol was precipitated by dry hydrogen chloride. The nearly white precipitate resembles the hydrobromide of chlormethenylaminophenol in every respect, except in having a slight tinge of color, due to the fact that perfectly pure and colorless brommethenylaminophenol was not used, on account of the difficulty of preparing it. The new salt melts, with decomposition, at  $155^\circ$ , which is also the melting-point of the hydrobromide of the chlor-body. The melting-point of a mixture of the two freshly prepared salts is also  $155^\circ$ . The new body is decomposed at once by water, *hydrobromic acid being chiefly split off*, with only traces of hydrochloric acid.

	Substance.	Calculated for $\text{C}_7\text{H}_5\text{NOBrCl}$ (one mol. of acid) cc. tenth- normal alkali.	Found.
	Gram.		cc.
I.	0.3414	14.56	12.83
II.	0.2580	11.00	10.68
III.	0.2279	9.72	9.42

The filtrate from analysis I. was precipitated by silver nitrate and a portion of the silver halide reduced to silver.

I. 0.2195 gram of the dry silver salt gave 0.1301 gram Ag. Another filtrate from some freshly prepared hydrochloride of the brom-body treated with water, was precipitated with silver nitrate.

II. 0.3967 gram of the dry silver salt gave 0.2299 gram Ag.

	Calculated for AgCl.	Calculated for AgBr.	I. Found.	II.
Halogen	24.73	42.55	40.73	42.05

As evidence of the identity of the hydrobromide of chlor-methenylaminophenol and the hydrochloride of brommethenylaminophenol we have the agreement in physical properties and melting-point and the fact that their mixture melts at the same temperature; but, since the bodies melt with some decomposition, it does not necessarily follow that their identity is absolutely proved by this latter fact as would be the case with bodies that melt without decomposition. However, the behavior with water, by which both split off chiefly hydrobromic acid with only traces of hydrochloric acid, is a fact which is inexplicable on any ground except the identity of the two bodies. The identity of these bodies justifies, therefore, the constitutions already ascribed to them; all of the halogen is consequently attached to carbon. That, moreover, these bodies are true salts was shown by the preparation of other salts and by obtaining ionic reactions in aqueous solutions.

*Chlormethenylaminophenol Nitrate*,  $\text{O.C}_6\text{H}_4\text{---NH.C.Cl.ONO}_2$ .  
 $\text{L-----L}$

Seidel states<sup>1</sup> that with concentrated nitric and hydrochloric acids chlormethenylaminophenol gives beautiful crystalline salts; but he does not give analyses nor further data, proving that these are really salts of chlormethenylaminophenol. The nitrate is readily obtained by treating the oil (0.3 to 0.4 gram) with 10 cc. of nitric acid (sp. gr. 1.28) at 0°. The oil dissolves and white crystals separate at once. These were quickly drained on a platinum cone with the aid of a pump,

<sup>1</sup> J. prakt. Chem. [2], 42, 455.



rubbed on a clay plate for a minute or two, and then dried over sulphuric acid in a vacuum, for 30 to 40 minutes. If the nitric acid is too concentrated or is allowed to remain in contact with the crystals too long, or if the temperature is allowed to rise much above  $0^{\circ}$  the salt becomes yellow, apparently on account of nitrification. The nitrate forms beautiful white crystals, which become yellow and finally brown on being kept a few hours in a desiccator. In contact with water the salt suffers complete hydrolysis into chlormethenylaminophenol and nitric acid. The analysis was made by bringing the dried crystals into a large, tared, wide-mouthed weighing-bottle, weighing quickly, then adding water and a drop of methyl orange and titrating with  $\frac{N}{10}$ -alkali.

	Substance. Gram.	Calculated for $C_9H_4ClNO.HNO_3$ . cc. tenth-normal alkali.	Found. cc.
I.	0.2592	12.0	11.8
II.	0.3974	18.4	19.0

The substance used in analysis II. had become slightly yellow; that in I. was pure white. A test of the solutions, after titrating in the above analysis, showed only traces of chlorine.

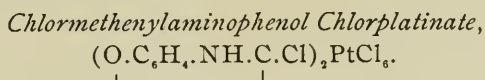
*The Action of Hydrochloric Acid on Chlormethenylaminophenol.*

When chlormethenylaminophenol is treated with cold concentrated hydrochloric acid it dissolves very readily and the oil separates out unchanged if water is added immediately. The solution in concentrated hydrochloric acid gives no crystals at once, but after standing an hour at  $0^{\circ}$  white crystals are deposited in considerable quantity. These have all the properties of carbonylaminophenol; they are not soluble in water nor are they decomposed by water, but dissolve readily in alkalies with acids. The alkaline solution gives white crystals, containing no chlorine, which are undoubtedly carbonylaminophenol. Even by the use of a solution of hydrochloric acid saturated at  $0^{\circ}$ , it was not possible to obtain the hydrochloride in the solid form. It is therefore probable that Seidel mistook the crystals of carbonylaminophenol, for those of the hydrochloride of chlormethenylaminophenol. That the salt exists in solution, being very soluble, was shown by the action of nitric acid on a freshly prepared



solution of the hydrochloride, and by the formation of a chlorplatinate.

A few drops of chlormethenylaminophenol were dissolved in about two volumes of concentrated hydrochloric acid. No crystals were formed, even on cooling the solution with ice and salt; the addition of nitric acid (sp. gr. 1.28) caused an immediate heavy white precipitate, which was undoubtedly the nitrate, since on the addition of water the crystals decomposed, leaving an oil—chlormethenylaminophenol. The formation of the nitrate in this way must be considered a true ionic reaction, and shows clearly that the bodies under discussion are true salts.



0.5 gram of chlormethenylaminophenol was dissolved in about 4 cc. of ice-cold concentrated hydrochloric acid and added to a solution of 0.5 gram of platinic chloride dissolved in 3 cc. of concentrated hydrochloric acid. After ten minutes the ice-cold solution had deposited a considerable quantity of orange-colored crystals. These were drained on a platinum cone, pressed out quickly on a clay plate, and dried over sulphuric acid. The crystals are stable in the absence of water, but the latter quickly decomposes the body into its constituents.

0.0529 gram gave 0.0141 gram Pt.

0.2334 gram gave 0.0619 gram Pt.

	Calculated for $(\text{C}_7\text{H}_5\text{ClINO})_2\text{PtCl}_6$ .	I.	Found.	II.
Pt	26.79	26.69		26.52

## PART II.

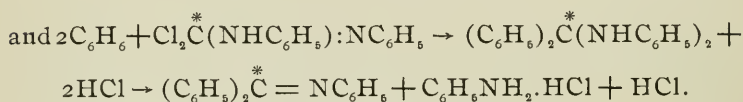
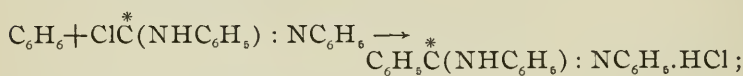
### *The Hydrochlorides of Carbodiphenylimide.*<sup>1</sup>

Carbodiphenylimide unites with hydrochloric acid, as Lengfeld and Stieglitz have found,<sup>2</sup> in two proportions; namely, to form the monohydrochloride,  $\text{C}(\text{C}_6\text{H}_5\text{N})_2\text{.HCl}$ , and the dihydrochloride,  $\text{C}(\text{C}_6\text{H}_5\text{N})_2\text{.2HCl}$ . From the fact that the monohydrochloride gives with sodium ethylate, smoothly

<sup>1</sup> Preliminary reports: Ber. d. chem. Ges., 30, 1090, 1682.

<sup>2</sup> This JOURNAL, 17, 107.

and quantitatively, ethyl isocarbanilide,  $C_2H_5OC(NHC_6H_5) : NC_6H_5$ , Lengfeld and Stieglitz<sup>1</sup> have thought it quite probable that, in the monochloride, the chlorine is bound to carbon and not to nitrogen; that it has consequently the constitution,  $Cl.C(NHC_6H_5) : NC_6H_5$ . Similarly, in the dihydrochloride, one, at least, and perhaps both chlorine atoms are bound to carbon thus:  $ClC(NHC_6H_5) : NC_6H_5.HCl$  or  $Cl_2C(NHC_6H_5)_2$ . In the hope of obtaining further evidence on this point, I have studied the action of the above hydrochlorides on benzene, in the presence of aluminium chloride. According to the view just expressed, it seemed possible, in this way, to obtain benzamidine (or benzophenone) derivatives,<sup>2</sup> according to:



<sup>1</sup> *Loc. cit.*; and Stieglitz: Ber. d. chem. Ges., 28, 537.

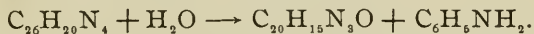
<sup>2</sup> Since Friedel and Crafts' syntheses with aluminium chloride involve, almost universally, the use of an alkyl or acyl haloid—that is, substances containing the group  $CCl$ , or its equivalent, it is thought that the reaction can be used to prove the presence of such a  $CCl$  group, in a chloride of doubtful constitution. This method of proof had, in fact, been previously used, most notably by Gattermann (Ann. Chem. (Liebig), 244, 47), in the closely allied case of the hydrochlorides of the isocyanates. According to their action on benzene derivatives, in the presence of aluminium chloride, they have been generally assumed to be chlorformanilides (*Vide*, Meyer and Jacobson: Lehrbuch, Vol. II., p. 199; Richter-Anschütz, 8th ed., Vol. II., p. 76)



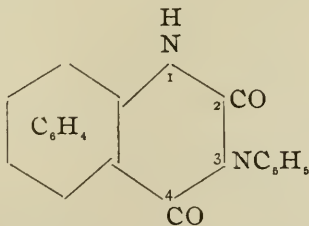
In fact, in their action on benzene, in the presence of aluminium chloride, they resemble substances which undoubtedly have a similar constitution, such as chlorformmethylanilide,  $RNCH_3.COCl$ . In the few cases where Friedel and Crafts' synthesis has succeeded without the use of an alkyl or acyl haloid—for instance, with phenyl isocyanate (Leuckart: Ber. d. chem. Ges., 18, 873) and with ethylene (Balsen: Bull. Soc. chim., 31, 541), it appeared most probable that such haloids were first formed by the addition of hydrogen chloride, which is always present (Leuckart: *Loc. cit.*; Gattermann: *Loc. cit.*).

The two most important interpretations of Friedel and Crafts' reaction agree with this conclusion: the older one (Friedel and Crafts: Ann. Chim. [6], 14, 457; Meyer u. Jacobson: Lehrbuch, II, 98) requiring a chlor-carbon group ( $CCl$ ) to react with the supposed intermediate organic derivative of aluminium chloride, *e.g.*,  $C_6H_5.Al_2Cl_5$ ; the new and interesting view of Nef (Ann. Chem. (Liebig), 298, 222) ascribing the condensation to the addition of phenyl and hydrogen ( $C_6H_5$  and  $H$ ) to the nascent double bonds of unsaturated derivatives, and thus postulating the presence of the same chlor-carbon group, to make a "nascent double bond" at all possible.

However no benzamidine nor benzophenone derivatives are formed. The chief product of the reaction is a yellow base, of the composition  $C_{26}H_{20}N_4$ , the constitution of which has been established by a thorough study of its reactions, its decomposition-products, and finally by its direct synthesis. The results leave no doubt that a Friedel and Crafts' condensation actually takes place involving the carbon atom marked with a star ( $C^*$ ); only instead of attacking the benzene itself, it enters one of the benzene nuclei of a second molecule of carbodiphenylimide. The composition of the new body is the same as that of carbodiphenylimide itself, but preliminary determination showed the body to have double the molecular weight of carbodiphenylimide. It has therefore the composition  $C_{26}H_{20}N_4$ . Several polymers of carbodiphenylimide are described in the literature;<sup>1</sup> but the body obtained by the action of aluminium chloride differs markedly from all of these and from carbodiphenylimide itself. The body  $C_{26}H_{20}N_4$  is a base, forming yellow crystals, which dissolve readily in dilute hydrochloric acid, to form a yellow solution, that soon becomes colorless. Alkalies precipitate from the colorless solution a white base, having the composition  $C_{20}H_{16}N_3O$ , while the aqueous solution contains aniline. Saponification of an aniline group has therefore taken place:



By further saponification of the substance  $C_{20}H_{16}N_3O$  by prolonged heating, in a sealed tube, with concentrated hydrochloric acid, a good yield of a body  $C_{14}H_{10}N_2O_2$ , which proved to be identical with the 3-phenyl-2-4-diketotetrahydroquinazoline of Busch<sup>2</sup> and Paal,<sup>3</sup>

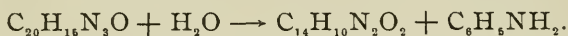


<sup>1</sup> Weith: Ber. d. chem. Ges., 7, 10; Schall: *Ibid.*, 25, 2886; Cf. Von Miller u. Plöchl: *Ibid.*, 28, 1004.

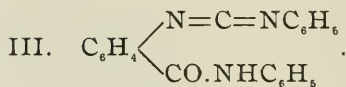
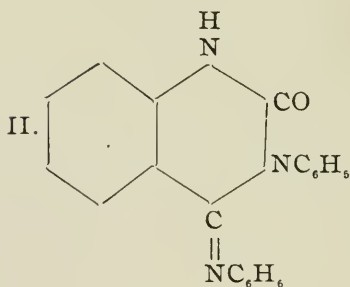
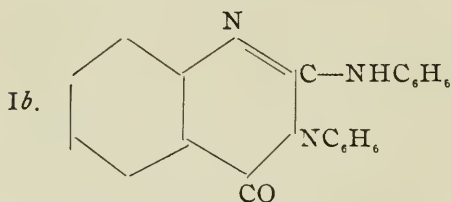
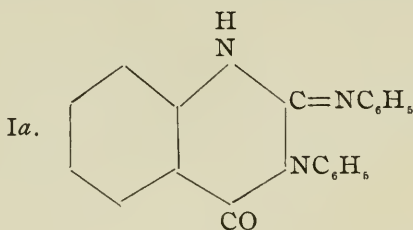
<sup>2</sup> J. prakt. Chem., 51, 265.

<sup>3</sup> Ber. d. chem. Ges., 27, 978.

was obtained, and at the same time aniline was formed. The action of concentrated hydrochloric acid on the white base,  $C_{20}H_{16}N_3O$ , is therefore expressed by the equation :



The compound  $C_{20}H_{16}N_3O$  must consequently have the constitution expressed by one of the following structural formulas:



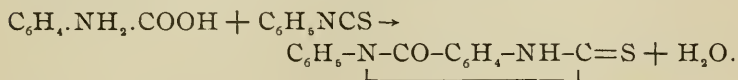
Formula III is excluded by the following properties of the body : (1) it is a strong base soluble in dilute acids ; (2) it remains unchanged when boiled with concentrated hydrochlo-

ric acid, as also when boiled with aniline. *Ia* and *Ib* differ from II only in the position of the aniline group attached to the quinazoline ring. Since the aniline group in position 2 (*Ia* or *b*) forms a derivative of triphenylguanidine, which is very stable toward saponifying agents, while in position 4 (II), we have a derivative of *s*-benzenyldiphenylamidine, which is readily saponified to benzanilide,<sup>1</sup> formula I (*a* or *b*) was supposed to be the more probable one, and this view was tested by preparing a body of the composition and constitution I. It proved to be identical with the white base,  $C_{20}H_{16}N_3O$ . The compound is, therefore, either 2-phenylimido-3-phenyl-4-ketotetrahydroquinazoline, *Ia*; or 2-phenyl-amido-3-phenyl-4-ketodihydroquinazoline, *Ib*.

Two substances corresponding to *Ia* and *Ib* are so closely related and pass over so readily into one and the same form that only one form is usually, if not always, known. Experiments will be described below, the object of which is to distinguish between these two forms.

With methyl iodide, the body gives the 1(N) methyl derivative, indicating, perhaps, formula *Ia*, on which account, to avoid the duplication of cumbersome names, that of formula *Ia* will be used in referring to the body and its derivatives. As, however, addition of the methyl iodide to the double bond between carbon and nitrogen, and subsequent splitting off of hydrogen iodide, may take place instead of direct substitution, this reaction is not free from objection, as a means of determining constitution, so that formula *Ib* is not absolutely excluded.

The synthetic proof of the constitution of the white base,  $C_{20}H_{16}N_3O$ , was furnished in the following manner: From anthranilic acid and phenyl mustard-oil, *o*-phenylthioureido-benzoic acid was prepared. The latter, by loss of water, readily gives 2-thio-3(N)-phenyl-4-ketotetrahydroquinazoline:



This compound, as also its thio-ether, 2-ethylthio-3(N)-phenyl-4-ketodihydroquinazoline, proved to be unusually in-

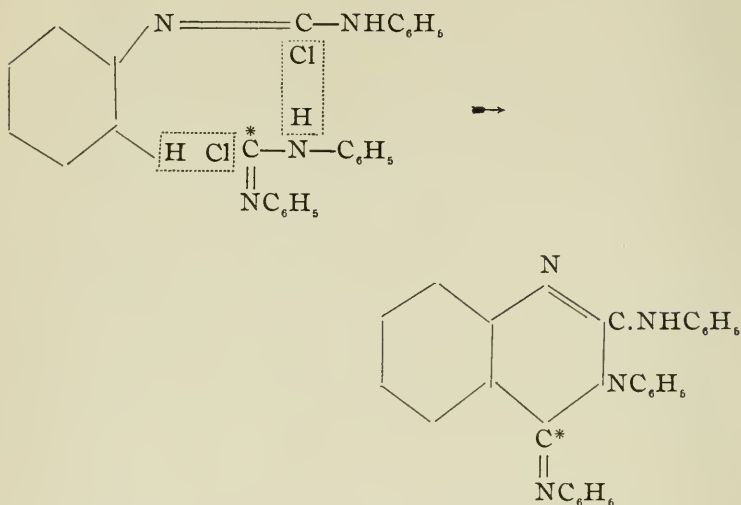
<sup>1</sup> Wallach: Ann. Chem. (Liebig), 184, 85.







chloride of carbodiphenylimide may be represented in the following simple manner :



On the basis of the prevalent views of the Friedel and Crafts' synthesis,<sup>1</sup> the entrance of the carbon atom C\* into the benzene ring, by the action of aluminium chloride, is in the best agreement with the views of Stieglitz and Lengfeld that in the monohydrochloride of carbodiphenylimide the chlorine is bound to carbon ; that it is therefore to be regarded as chlor-formyldiphenylamidine,  $\text{ClC}(\text{NHC}_6\text{H}_5):\text{NC}_6\text{H}_5$ .

By using carbodiphenylimide, instead of its hydrochloride, the yield of the yellow base is very materially reduced, being only one-tenth as large as that obtained from the monochloride (5 per cent. instead of 50 per cent. of the theoretical yield) and here, as in Leuckart's results with phenyl isocyanate,<sup>2</sup> benzene and aluminium chloride, the formation of any of the quinazoline compounds at all may be ascribed to the liberation of some hydrogen chloride, which would convert the carbodiphenylimide into the monochloride.

That the chlorine atom in question becomes attached to car-

<sup>1</sup> *Vide* note p. 132.

<sup>2</sup> *Loc. cit.*

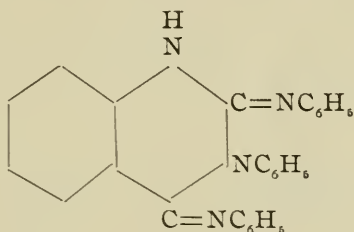
bon *before* the possible saturation of the free nitrogen valencies, by an excess of hydrogen chloride, as perhaps according to the equation,

$C(:NC_6H_5.HCl)_2 + HCl \rightarrow Cl.C(:NC_6H_5.HCl)(NHC_6H_5.HCl)$ ,  
is proved by the fact that an excess of hydrogen chloride must be avoided in order to accomplish the formation of the quinazoline compound.

#### EXPERIMENTAL PART.

*The Action of Aluminium Chloride on the Chlorides of Carbodiphenylimide.*

*2-4-Diphenylimido-3(N)-phenyltetrahydroquinazoline,*



Carefully dried hydrogen chloride was passed into a solution of freshly prepared carbodiphenylimide (10 grams) in benzene (70 cc.) free from thiophene until a heavy precipitate was obtained. As Lengfeld and Stieglitz<sup>1</sup> have shown, this precipitate consists of a mixture of the two chlorides of carbodiphenylimide, while the benzene solution still contains unchanged imide in solution. The mixture so obtained was diluted with 100 cc. of pure carbon bisulphide; heated to boiling; and 10 grams of aluminium chloride added, in portions of 2 grams in the course of three-quarters of an hour. After heating for a quarter of an hour longer, the nearly colorless benzene and carbon bisulphide solution, which still contained a little unchanged carbodiphenylimide, was poured from the dark-brown mass that had separated during the reaction. The latter was treated with dilute sodic hydrate and with water to remove aluminium compounds; and the yellow resi-

<sup>1</sup> This JOURNAL, 17, 107.

due, excepting a small insoluble portion, was dissolved in carbon bisulphide, in which the product is now very easily soluble. On evaporating the solution at the ordinary temperature, yellow crystals of 2-4-diphenylimido-3(N)-phenyltetrahydroquinazoline separated, the amount of which was increased by adding alcohol.

The body was purified by dissolving in benzene and adding ligroin (b. p. 40–60°). With a small amount of ligroin, a small quantity of sulphur-yellow, rhombic plates ( $\beta$ -form), melting at 184°, was obtained, while the filtrate with more ligroin gave a far greater amount of yellow prisms ( $\alpha$ -form), melting at 171°.

0.2097 gram of the  $\alpha$ -form gave 0.6150 gram  $\text{CO}_2$ , and 0.0966 gram  $\text{H}_2\text{O}$ .

0.1062 gram of the  $\alpha$ -form gave 0.3141 gram  $\text{CO}_2$ , and 0.0544 gram  $\text{H}_2\text{O}$ .

0.1976 gram of the  $\alpha$ -form gave 24.7 cc. of  $\text{N}_2$  at 17.5° and 752.4 mm.

	Calculated for $\text{C}_{13}\text{H}_{10}\text{N}_2$ or $\text{C}_{26}\text{H}_{20}\text{N}_4$ .	I.	Pound. II.	III.
C	80.41	80.00	80.66	....
H	5.15	5.20	5.68	....
N	14.44	....	....	14.38

As has been mentioned, the yield of the above body depends, to a great extent, upon the amount of hydrogen chloride present during the reaction with aluminium chloride. Under favorable conditions the yield is about 50 per cent. An excess of hydrogen chloride must be avoided. In cases in which very much more than one equivalent of hydrogen chloride was passed into the benzene solution of carbodiphenylimide very little, or with a great excess even none, of the quinazoline resulted. The best yield was obtained by dissolving equivalent quantities of carbodiphenylimide and its pure dry dihydrochloride<sup>1</sup> in benzene, thus securing exactly one equivalent of hydrogen chloride. This procedure is unnecessary if, in the preparation of the chloride, the current of hydrogen chloride is stopped before any of the heavy precipitate first formed begins to dissolve, as at this point

<sup>1</sup> Lengfeld and Stieglitz: This JOURNAL, 17, 107.

approximately one molecule of the gas has been absorbed. It has been found that the best method of separating the body from the by-products, which are chiefly unchanged carbodiphenylimide, polymeric carbodiphenylimide and carbanilide, the latter being formed by the action of water on carbodiphenylimide, consists in treating the mixture, left after removing aluminium compounds, as above described, with cold alcohol in small portions, and dissolving the residue, which is chiefly the new body, in hot acetone and adding 80 per cent. alcohol. On standing, most of the substance separates in prisms of the  $\alpha$ -form.

The action of aluminium chloride either on free carbodiphenylimide or on its pure dichloride, in the presence of benzene and carbon bisulphide, gives very much smaller yields of the body,  $C_{26}H_{20}N_4$ , than when the reaction is carried out in the presence of approximately *one* equivalent of hydrogen chloride.

Two grams of pure freshly made and freshly distilled carbodiphenylimide were dissolved in benzene and carbon bisulphide, and the solution treated with aluminium chloride in the usual manner. From the reaction-product 0.107 gram ( $=5\frac{1}{2}$  per cent.) of the body,  $C_{26}H_{20}N_4$ , was obtained.

Five grams of the pure dihydrochloride of carbodiphenylimide treated, in the presence of benzene and carbon bisulphide, with aluminium chloride in the usual way, gave 0.47 gram ( $=12\frac{1}{2}$  per cent.) of the yellow body  $C_{26}H_{20}N_4$ . The theoretical significance of these results has already been discussed.

The molecular weight determination of the  $\alpha$ -form of the yellow body,  $C_{26}H_{20}N_4$ , by the lowering of the freezing-point of benzene, showed the body to have the double formula :

	Benzene. Grams.	Substance. Gram.	Lowering.	Mol. weight. Found.
I.	35.62	0.3356	$0.136^\circ$	347
	35.62	0.6086	$0.240^\circ$	356
II.	35.44	0.5494	$0.223^\circ$	348
	35.44	0.8184	$0.335^\circ$	354

Calculated for  $C_{13}H_{10}N_2$ , 194 ; for  $C_{26}H_{20}N_4$ , 388.

The determination by the elevation of the boiling-point of chloroform,<sup>1</sup> led to the same conclusion :

Chloroform. Grams.	Substance. Gram.	Elevation.	Mol. weight. Found.
28.7	0.6242	0.223°	360
28.7	0.9904	0.344	372

Analysis of the  $\beta$ -form showed that it has the same composition as the  $\alpha$ -form :

0.1830 gram of the  $\beta$ -form gave 24.2 cc.  $N_2$  at 26° and 745.5 mm.

Calculated for $C_{13}H_{10}N_2$ or $C_{26}H_{20}N_4$ .		Found.
N	14.44	14.48

The molecular weight determination of the  $\beta$ -form, by the freezing-point method in benzene, also showed the double formula to be the correct one :

Benzene. Grams.	Substance. Gram.	Lowering.	Mol. weight found.
20.3	0.4046	0.271°	368
20.3	0.6701	0.466°	354

The two forms ( $\alpha$  and  $\beta$ ) are converted into each other with the greatest ease. When the  $\alpha$ -form is heated to its melting-point and allowed to cool slowly, it crystallizes in rhombic plates of the  $\beta$ -form, and these when heated again melt sharply at 184°. The  $\alpha$ -form dissolves in benzene very readily, but the clear solution soon deposits rhombic plates of the  $\beta$ -form, melting at 184°. Either form, crystallized from any of the following solvents : alcohol, acetone, ligroin, ethyl acetate, acetoacetic ester, acetic anhydride or aniline, gives *only* the  $\alpha$ -form. The fact that crystallization from benzene gave one form, while from alcohol the other was obtained, caused a determination of the solubility of each form, in each of these solvents, to be made. At the temperature of the room, a saturated solution in benzene contains :

$\alpha$ -Form (prisms). Per cent.	$\beta$ -Form (plates). Per cent.
14.2	7.3

A saturated solution in alcohol contains :

<sup>1</sup> Molecular elevation taken as 36.6°; Beckmann: Ztschr. phys. Chem., 8, 227.



$\alpha$ -Form.  
Per cent.  
0.17

$\beta$ -Form.  
Per cent.  
0.24

The result shows that, in both cases, it is the less soluble form, which crystallizes from the solvent. Finding later that the  $\alpha$ -form is obtained by crystallizing from acetone, it was predicted that this form would be less soluble in this solvent. Experiments confirmed this.

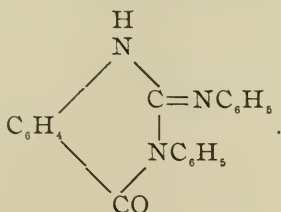
A saturated solution in acetone contains :

	$\alpha$ -Form. Per cent.		$\beta$ -Form. Per cent.
I.	5.73	III.	6.74
II.	5.89	IV.	7.33

The  $\beta$ -form dissolves in acetone quite readily, but the  $\alpha$ -form separates so quickly, that in determination III, this began to take place during the filtration; hence the low result.

The body  $C_{26}H_{20}N_4$  is remarkably stable towards heat, distilling unchanged in a vacuum above  $340^\circ$ . The distillate solidifies to an amber-like amorphous mass, which has no definite melting-point, beginning to soften at about  $100^\circ$ . On standing and especially on warming and also by the use of solvents, the amorphous substance is readily converted, according to the conditions, into the  $\alpha$ - or  $\beta$ -crystalline form. The results of these experiments led to the conclusion that the two forms are physical or crystallographic modifications of the same substance. On the other hand a most surprising difference was found in the behavior of benzene solutions of the two forms towards phenyl isocyanate, as will be discussed later, a fact which would seem to point to a chemical difference between the two forms.

*2-Phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline,*



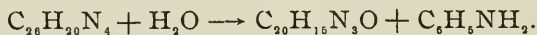
Both forms of the yellow body,  $C_{20}H_{20}N_4$ , dissolve in dilute hydrochloric acid, forming a bright yellow solution which becomes perfectly colorless on standing in the cold several hours, or in a few minutes at the boiling-point. Alkalies now precipitate from the colorless solution a white base, which has been shown to be 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline,  $C_{20}H_{16}N_3O$ , while aniline remains in the aqueous solution. The aniline was identified, after distilling it off with steam, by the bleaching-powder reaction, by the isonitrile test, and by conversion into benzanilide. The latter melted at  $160^\circ$ , and the melting-point remained unchanged on mixing with pure benzanilide, made in the usual way. The new body is a decided base, dissolving easily in dilute acids, from which alkalies precipitate it unchanged. Recrystallized from alcohol, it is obtained in colorless needles, melting at  $163^\circ$ . It is easily soluble in benzene, chloroform, and carbon bisulphide; less soluble in alcohol and ether, and almost insoluble in low-boiling ligroin and water.

0.1225 gram gave 0.3460 gram  $CO_2$ , and 0.0545 gram  $H_2O$ .

0.1042 gram gave 12.65 cc.  $N_2$  at  $23^\circ$  and 759.7 mm.

	Calculated for $C_{20}H_{16}N_3O$ .	Found.
C	76.62	77.05
H	4.82	4.98
N	13.45	13.75

The reaction has taken place according to the following equation :



A quantitative experiment gave an almost theoretical yield of the body  $C_{20}H_{16}N_3O$ ,—77.9 instead of 80.6 per cent.

The body,  $C_{20}H_{16}N_3O$ , is saponified but very slowly by boiling with concentrated hydrochloric acid or with alcoholic potash. For the further saponification, 5.3 grams of the substance, with 12 cc. of concentrated hydrochloric acid, was heated in a sealed tube seven hours at  $160^\circ$ – $180^\circ$ . On cooling, large colorless plates (3.1 grams) had formed. These were separated from the brown acid solution, which latter gave with alkali 0.4 gram of the unchanged base. The alka-

line filtrate on extraction with ether gave aniline, which was identified by its boiling-point,  $183^{\circ}$ , and by the melting-point  $160^{\circ}$ , of the benzanilide formed by treating it with benzoyl chloride. The melting-point was not changed by mixing with synthetic benzanilide.

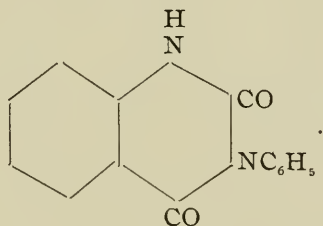
The above-mentioned colorless crystals, after recrystallization from boiling alcohol, formed needles melting at  $272^{\circ}$ .

0.1849 gram gave 0.4775 gram  $\text{CO}_2$ , and 0.0718 gram  $\text{H}_2\text{O}$ .

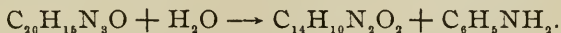
0.1303 gram gave 13.8 cc.  $\text{N}_2$  at  $16^{\circ}$  and 742.1 mm.

	Calculated for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$ .	Found.
C	70.54	70.44
H	4.23	4.34
N	11.79	12.09

The composition and melting-point are those of 2-4-diketo-3(N)-phenyltetrahydroquinazoline,<sup>1</sup>



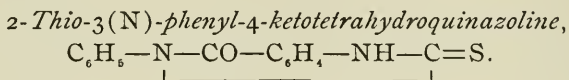
The analyzed body, like that described by Busch and by Paal, shows in alkaline solution an extraordinary blue fluorescence. The phenomenon is especially beautiful in dilute solution; in stronger solutions in the presence of much alkali it is much fainter. As a complete proof of the identity of the body obtained by me, with that of Busch and Paal, the body was made according to the directions of the latter from anthranilic acid and phenyl isocyanate. By mixing the quinazoline bodies obtained in both ways the melting-point ( $273^{\circ}$ ) remained unchanged; all other properties were also identical. Hence it follows that the saponification has taken place thus:



The method of synthesis and its properties leave no doubt

<sup>1</sup> Busch: J. prakt. Chem. [2], 51, 265; Paal: Ber. d. chem. Ges., 27, 978.

concerning the constitution of 2-4-diketotetrahydroquinazoline—the body  $C_{14}H_{10}N_2O_2$ . The constitution of the body,  $C_{20}H_{16}N_2O$ , must therefore be represented by one of the formulas Ia, Ib, II or III, page 134. As has already been mentioned, formula III is excluded by the properties of the body, while, between I(a or b) and II, the former was given the preference and the constitution proved by preparing such a compound synthetically. It was found to be identical with the base  $C_{20}H_{16}H_2O$ . The first step in the synthesis was the preparation of



Anthranilic acid (10 grams) was dissolved in 100 cc. of alcohol and 50 cc. of water, containing a little over one molecule of potassic hydrate, and phenyl mustard-oil (9 grams = 1 mol.) added. Most of the mustard-oil goes into solution at once. After standing two or three hours, with occasional shaking, the reaction is complete. Without alcohol the action is extremely slow, but with an excess of alcohol much phenylthiourethane is formed. Water is added after the reaction is complete. The solution is filtered from a small oily precipitate, when necessary, and saturated with carbon dioxide. The nearly white heavy granular precipitate, which forms very slowly, is complete only after several hours. For further purification the product was dissolved in dilute alkali and again treated with carbon dioxide, which now causes a rapid separation of a voluminous precipitate.

By its analysis and behavior, the body was shown to be the above-mentioned thioquinazoline.<sup>1</sup> It is a very weak acid, like all similar thioamides; it dissolves in alkalies (without fluorescence), and is then precipitated immediately by carbon dioxide; it is difficultly soluble in most organic solvents, and crystallizes from a mixture of alcohol and acetone in almost colorless rectangular plates, which melt without decomposition above 300°.

0.1540 gram gave 15.7 cc.  $N_2$  at 23° and 748.7 mm.

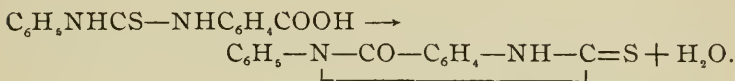
<sup>1</sup> Vide Stewart: J. prakt. Chem. [2], 49, 415.

	Calculated for $C_{14}H_{10}N_2SO$ .	Found.
N	11.05	11.38

In the action of phenyl mustard-oil on anthranilic acid, the first product is evidently *o*-phenylthioureïdobenzoic acid :



The latter is stable in alkaline solution, but in the small quantity in which it is liberated in the solution by the weaker carbonic acid, it loses water, forming the quinazoline derivative :



The formation of 2-4-diketo-3(N)-phenyltetrahydroquinazoline, by evaporating a solution of the ammonium salt of phenylureïdobenzoic acid,<sup>1</sup> must depend in a similar manner upon the gradual liberation of the acid by the slow decomposition of the salt in solution. The intermediate thioureïdobenzoic acid may be isolated by treating the reaction-product of anthranilic acid and mustard-oil, with hydrochloric acid instead of carbonic acid. This causes an immediate precipitate, which contains some quinazoline. To remove the latter the precipitate is dissolved in aqueous sodium bicarbonate, in which the quinazoline is insoluble, quickly filtered, and again precipitated with hydrochloric acid. The thioureïdo acid so prepared, after being dried on a clay plate, was crystallized by dissolving in acetone and adding ligroin (40°-60°). The colorless needles are undoubtedly *o*-phenylthioureïdobenzoic acid. The acid melts with decomposition at 185°-190°, when plunged into the hot bath. It is readily soluble in sodium bicarbonate, and on treating the solution with carbon dioxide the thioquinazoline slowly separates out as before.

By oxidation with potassium permanganate Busch<sup>2</sup> converted 2-thiotetrahydroquinazoline into 2-4-diketotetrahydroquinazoline. Similarly, 2-thio-3(N)-phenyl-4-ketotetrahy-

<sup>1</sup> Paal : *Loc. cit.*

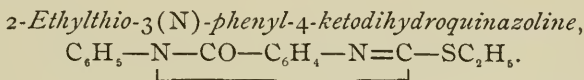
<sup>2</sup> J. prakt. Chem. [2], 51, 128.



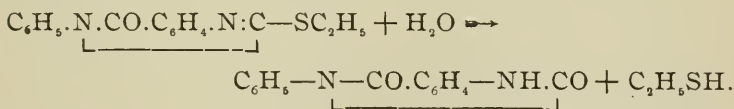


Since in the thio-body the sulphur atom is in position 2, it follows that the aniline group is also in 2 and not in 4; that, therefore, formula I(*a* or *b*), page 134, must represent the body  $C_{20}H_{16}N_3O$ .

As the thio-ethers<sup>1</sup> of thioanilides are especially reactive toward aniline, the ethyl ether of the above thio-body was made and treated with aniline, in the hope of obtaining a better yield of the body,  $C_{20}H_{16}N_3O$ , synthetically.



2-Thio-3(N)-phenyl-4-ketotetrahydroquinazoline was covered with alcohol, brought into solution by 30 per cent. potassic hydrate, and somewhat more than the calculated amount of ethyl iodide added. The solution after boiling half an hour and filtering from a slight residue gave, on cooling, long colorless needles of the thio-ether, the amount of which was increased to an almost theoretical yield by evaporating the mother-liquor. After a crystallization from somewhat dilute alcohol the substance is pure. It forms long, colorless needles melting at 114°. By boiling with dilute hydrochloric acid, ethylmercaptan (recognized by its odor) was given off, and the residue gave, with dilute alkali, a solution having the characteristic violet fluorescence of 2-4-diketo-3(N)-phenyltetrahydroquinazoline:



The method of preparation and the behavior with hydrochloric acid show that the body has the constitution given.

0.1592 gram gave 14.25 cc.  $N_2$  at 24° and 748 mm.

	Calculated for $C_{16}H_{14}N_2SO$ .	Found.
N	9.95	9.93

As a further means of confirming the constitution of my

<sup>1</sup> Wallach: Ber. d. chem. Ges., 12, 1061.

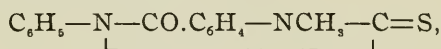
thio-ether,<sup>1</sup> I have also made the corresponding methyl ether,  $\text{C}_6\text{H}_5\text{—N—CO.C}_6\text{H}_4\text{.N:C—SCH}_3$ , in exactly the same way

as that by which the ethyl ether was obtained. It forms long needles melting at  $125^\circ$ , easily soluble in alcohol.

0.1032 gram gave 0.0888 gram  $\text{BaSO}_4$ .

	Calculated for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{SO}$ .	Found.
S	11.94	11.83

Boiled with dilute hydrochloric acid it is slowly saponified, giving methylmercaptan and leaving the diketoquinazoline. The isomeric 1(N)-methyl body, 1(N)-methyl-2-thio-3(N)-phenyl-4 ketotetrahydroquinazoline,



has recently been made by Fortmann,<sup>2</sup> from methylantranilic acid, and melts at  $288^\circ\text{--}289^\circ$ . There can therefore be no doubt as to the nature of the thio-ether obtained by me.

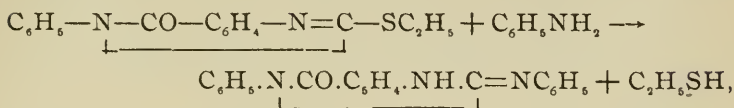
*The Action of Aniline on 2-Ethylthio-3(N)-phenyl-4-ketodihydroquinazoline.*

To accomplish a reaction with aniline 2-ethylthio-3(N)-phenyl-4-ketodihydroquinazoline must be heated in a sealed tube. 1 gram of the ether was heated to  $300^\circ$  for eight hours with 5 grams of aniline. On opening the tube the odor of mercaptan was very strong. After distilling off the excess of aniline, the larger part of the dark-red residue dissolved in hot dilute hydrochloric acid, forming a dark-green solution. By fractional precipitation with alkali a small amount of a dark-red mass was obtained which contains a dye that dissolves in alcohol forming a red solution, having a remarkable orange-colored fluorescence. Acids change the color to green. The dye has not yet been studied further. From the principal part of the precipitate with alkali, after decolorizing by boiling the alcoholic solution with animal charcoal, nearly colorless needles melting at  $162^\circ.5$  were obtained; these mixed with pure 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquin-

<sup>1</sup> *Vide* Ber. d. chem. Ges., 30, 1690.

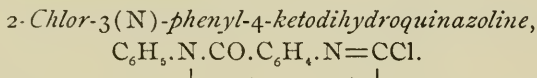
<sup>2</sup> J. prakt. Chem., 55, 132.

azoline (m. p. 163°) showed the same melting-point. The reaction,



has therefore occurred. The yield, about 10 per cent., was somewhat better than in the preceding synthesis, but still unsatisfactory.

The idea suggested itself that, by replacing sulphur in 2-thio-3(N)-phenyl-4-ketotetrahydroquinazoline by chlorine, a body could be obtained that would react readily and smoothly with aniline to give the body  $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$ . Such proved to be the case. By exactly the same method as that by which chlorimethenylaminophenol was obtained<sup>1</sup> from thio-carbaminophenol, the above thioquinazoline derivative yields the corresponding chloride.<sup>2</sup>



Five grams of the dry, finely powdered thio-body were suspended in 50 grams of dry chloroform, free from alcohol, and treated with carefully dried chlorine. The mixture warmed somewhat, but even with an excess of chlorine a large amount of a yellow body remained undissolved. The mixture was poured into water in small quantities and shaken vigorously, thus destroying the chloride of sulphur and causing the yellowish body to dissolve in the chloroform. After washing with dilute alkali and with water, and drying the chloroform solution with calcium chloride, the solvent was distilled off leaving the chlorquinazoline as a light-colored oil which soon crystallized in needles. The crystals, after washing with ether and drying, melt at 130°, but are not quite pure. For the analysis the body was distilled in a vacuum. It boils at about 245° at 15 mm. and the distillate forms a pure, white, crystalline mass, melting at 131°.5. It is easily

<sup>1</sup> *Vide*, p. 123.

<sup>2</sup> Cf. Gabriel : *Ber. d. chem. Ges.*, 29, 1306.

soluble in chloroform and benzene, less in alcohol and ether, and difficultly soluble in ligroin ( $40^{\circ}$ – $60^{\circ}$ ). From a solution in benzene the body is precipitated by ligroin in needles. It may be recrystallized from boiling alcohol unchanged,—a fact which shows how firmly the chlorine atom is held in the molecule.

An attempt to determine the chlorine according to Carius was unsuccessful. After heating for six hours at  $240^{\circ}$  and for four hours at  $340^{\circ}$  a considerable amount of an orange-colored compound, insoluble in acids, remained unoxidized. A chlorine determination was easily accomplished in a very short time by boiling, for thirty minutes, a solution of the weighed substance with 20 cc. of pure methyl alcohol in which 0.5 gram of sodium had been dissolved. The solution, from which common salt had separated, was diluted with water, acidified with nitric acid, and titrated with silver nitrate, according to Volhard.

0.1863 gram required 7.35 cc.  $\frac{N}{10}$   $\text{AgNO}_3$ .

0.4260 gram required 16.53 cc.  $\frac{N}{10}$   $\text{AgNO}_3$ .

	Calculated for $\text{C}_{14}\text{H}_9\text{N}_3\text{ClO}$ .	I.	Found.	II.
Cl	13.84	13.79		14.00

*2-Dichlor-3(N)-phenyl-4-ketotetrahydroquinazoline,*  
 $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}\cdot\text{Cl}_2$ .

Like chlormethenylaminophenol, the above analyzed monochlorquinazoline gives, with dry hydrogen chloride, a dichloride, which in all probability is to be represented by the above formula. Carefully dried hydrogen chloride was passed into a solution of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline in benzene. A white precipitate resulted which, after filtering and washing with ligroin as quickly as possible, was pressed on a clay plate for a minute or so and then dried in a vacuum over sulphuric acid. On opening the desiccator, a very little hydrochloric acid was noticed, showing slight decomposition. The substance melts at  $140^{\circ}$  with decomposition. In contact with water, it readily loses one molecule of acid, giving the original quinazoline chloride.

For the analysis the weighed substance was covered with water and titrated with alkali, methyl orange being used as an indicator.

0.2901 gram required 9.6 cc.  $\frac{N}{10}$  alkali.

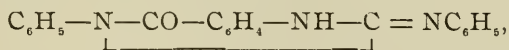
0.2800 gram required 9.0 cc.  $\frac{N}{10}$  alkali.

Cl	Calculated for	Found.	
	$C_{14}H_9N_2ClO.HCl.$	I.	II.
	12.09	11.73	11.40

In the preparation of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline from the thio-derivative, the yellowish body insoluble in chloroform remaining after the treatment with chlorine is undoubtedly the above dichloride.

*Synthesis of 2-Phenylimido-3(N)phenyl-4-ketotetrahydroquinazoline.*

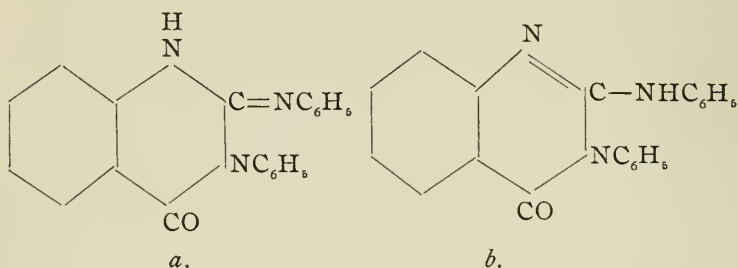
2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline dissolves readily in aniline, but the reaction with it goes on very slowly in the cold ; only after two days had the mixture solidified. At the boiling-point of aniline the reaction is complete in fifteen minutes ; on cooling the product solidifies to a crystalline mass, which dissolves readily in aqueous hydrochloric acid, with the exception of a small dark-colored residue. The nearly colorless filtrate gives with alkalis an almost white precipitate which, after recrystallization from alcohol, forms colorless needles melting at  $163^{\circ}$ . The body thus obtained was identical in every respect with 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline,



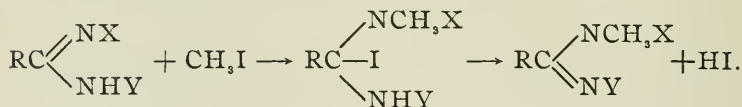
obtained by the saponification of the yellow base,  $C_{26}H_{20}N_4$ , which is formed by the Friedel and Crafts reaction from the hydrochloride of carbodiphenylimide. When the substances made in both ways are mixed there is no change in the melting-point. Thus the absolute identity of the substances is established. The new method of preparing 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline is much to be preferred to the old, as the yields in all of the transformations are

excellent. A large part of the substance used was prepared in this way.

This synthesis confirms the constitution already established by the other two syntheses from the thio-derivatives. The body,  $C_{20}H_{16}N_3O$ , has, therefore, one of the so-called tautomeric forms *a* or *b*:



The question still remained: Which of these two formulas is to be ascribed to the body in hand? The question is very much like that concerning the constitution of the amidines, the diazoamido bodies, etc. Of all these analogous bodies, experiment has shown that, with a very few doubtful exceptions, but one of the two possible forms exists. In his work on amidines, von Pechmann<sup>1</sup> has used the reaction with methyl iodide to determine the position of the "labile" hydrogen atom, assuming that the methyl group takes the place occupied by the hydrogen atom. This method is, however, not entirely free from objection, since it is possible that the methyl iodide may first be added to the double bond, just as hydrogen haloid is added to the double bond of the similarly constituted imido-esters; the loss of hydriodic acid would then give a body having the methyl attached to the nitrogen atom which originally held no hydrogen; thus,



Direct substitution of methyl for hydrogen would give

<sup>1</sup> Ber. d. chem. Ges., 28, 869, 2362.



$$\text{RC} \begin{array}{l} \diagup \text{NX} \\ \diagdown \text{NCH}_2\text{Y} \end{array}$$
 . The same amidine could thus give two iso-

meric methyl derivatives; in fact where X and Y are very similar, two alkyl derivatives are obtained by treating with alkyl iodide. The results of the action of methyl iodide admit of an ambiguous interpretation when viewed from the standpoint of Nef.<sup>1</sup> Here, besides the absorption of the amidine by methylene, an addition of hydrogen iodide to the double bond of the amidine may first take place leading to a rearranged product.

In the case of the diazoamido bodies H. Goldschmidt<sup>2</sup> has employed a reagent for determining the constitution with which the possibility of a rearrangement is excluded, namely, phenyl isocyanate, his leading thought being that, in reactions with phenyl isocyanate, all traces of moisture, acids, etc., can be excluded, which could cause the change of one form of these closely allied "tautomeric" substances into the other. Further, phenyl isocyanate cannot be absorbed by a double bond of the body whose constitution is to be determined; on the contrary, the only possible reaction is an absorption of the latter body by the isocyanate, giving a urea derivative, the determination of whose constitution fixes that of the compound in question. This excellent reagent was applied in the present investigation with the view of deciding between the two possible formulas *a* and *b* (p. 154) for the body  $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$ .

*The Action of Phenyl Isocyanate on 2-Phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline.*

The substances do not act readily in the cold nor by heating at  $150^\circ$  for one hour. The desired reaction took place, however, when 7 grams of the body  $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$  were dissolved in 80 cc. of dry benzene containing 2.6 grams of phenyl isocyanate and allowed to stand for eleven days in a well-corked flask placed in a desiccator which was kept in a light place. The solution, which had become somewhat brown, was treated with alcohol to convert the unchanged cyanate into easily soluble urethane, since by exposure to the air the

<sup>1</sup> Ann. Chem. (Liebig), 298, 202.

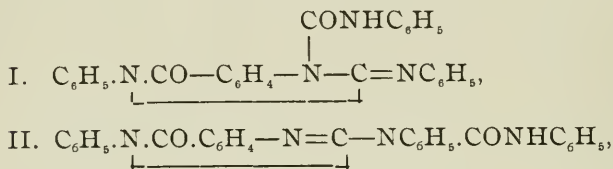
<sup>2</sup> Ber. d. chem. Ges., 21, 2557.

cyanate would absorb water with the formation of carbanilide, which would be difficult to remove. The benzene was distilled off in a vacuum and the viscous residue dissolved in 60-70 cc. of hot alcohol. From the brown solution a large amount of colorless crystals separated on cooling. These consist of a mixture of the unchanged basic body,  $C_{20}H_{15}N_3O$ , and the new urea. To remove the former the mixture was treated with dilute hydrochloric acid. The neutral insoluble residue by recrystallization from hot alcohol gave 3.2 grams of colorless needles, melting at  $127^\circ$ . According to its behavior and its analysis, the new substance is the expected urea.

0.1099 gram gave 13.2 cc.  $N_2$  at  $23^\circ$  and 742.2 mm.

	Calculated for $C_{27}H_{20}N_4O_2$ .	Found.
N	12.96	13.28

The urea must have either the constitution I. or II.



corresponding to the formulas *a* and *b* (page 154) respectively, for the body  $C_{20}H_{15}N_3O$ .

By heating to  $130^\circ$  the urea is completely decomposed into phenyl isocyanate and the body  $C_{20}H_{15}N_3O$ . The latter, after removing the cyanate in a current of air, was perfectly pure, and formed a white crystalline mass, having the correct melting-point,  $163^\circ$ . Its identification was established by mixing with the pure substance, when the melting-point remained unchanged.

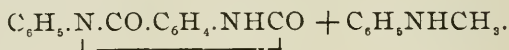
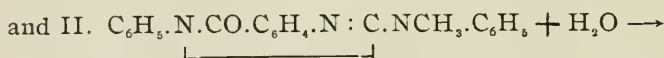
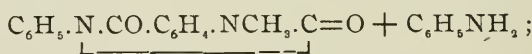
It was hoped that a urea of constitution II could be prepared by the following method, which would leave no doubt of its constitution, but all attempts were unsuccessful. 2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline and ethylisodiphenylurea<sup>1</sup> should react<sup>2</sup> to give a body of constitution II:

<sup>1</sup> Lengfeld and Stieglitz: Ber. d. chem. Ges., 27, 926.

<sup>2</sup> *Vide* paper by Dains soon to be published in The Journal of the American Chemical Society.



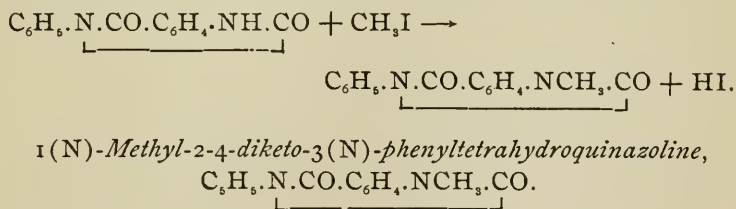
iodide, in which the quinazoline is easily soluble, were heated in a sealed tube to  $100^{\circ}$  for nine hours. The brown product was partly insoluble in the excess of methyl iodide. The latter was distilled off, and the residue dissolved in pure acetone, in which it is easily soluble. The acetone solution was treated with aqueous hydrochloric acid and much water added. A brick-red tar separated in small quantity, leaving a colorless solution of the bases, which were precipitated fractionally by alkali. After one crystallization from alcohol, the first fraction was the nearly pure unmethylated white base,  $C_{20}H_{15}N_3O$ , as was shown by its melting-point ( $162^{\circ}$ ), which changed to  $162^{\circ}.5$  by mixing with some of the pure body,  $C_{20}H_{15}N_3O$  (m. p.  $163^{\circ}$ ). The second fractional precipitate with alkali, after one crystallization from alcohol, melted at  $135^{\circ}$ – $140^{\circ}$ , and was evidently a mixture. The third fraction, which was small, after recrystallization from alcohol, melted at  $174^{\circ}$ . The new body, which was found to be the methyl derivative of the white base,  $C_{20}H_{16}N_3O$ , forms colorless needles melting at  $174^{\circ}$ , easily soluble in alcohol. The perfectly pure substance amounted to but 0.05 gram, but the experiment was not repeated to obtain sufficient for an analysis, as the constitution could be firmly established only by the saponification products. The two possible reactions are represented by :



It was finally established that the products of saponification are those given by reaction I.—aniline and 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline. The base melting at  $174^{\circ}$  produced by methylation of the white base (m. p.  $163^{\circ}$ ) must therefore be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline, and the white base itself

(m.p. 163°) is accordingly 2-phenylimido-3(N)-phenyl-4-keto-tetrahydroquinazoline.

The methylated body (m. p. 174°) was heated in a sealed tube with concentrated hydrochloric acid to about 180° for four hours. The product consisted of light-colored needles, insoluble in the acid. Water was added and the crystals filtered off. The filtrate gave no precipitate with alkali, showing the saponification to have been complete. The crystals are insoluble in dilute acids and alkalies, somewhat soluble in hot concentrated hydrochloric acid, and crystallize out on cooling. The crude saponification-product melted at 222°, and after dissolving in benzene and precipitating with ligroin (40°–60°), when the substance was obtained in nearly white needles, the melting-point was 223°. 2-4-Diketo-3(N)-phenyl-tetrahydroquinazoline, the product to be expected, if equation II, page 158, represented the saponification reaction, melts at 272° and is soluble in alkali. It was therefore thought that the substance melting at 223° must be its 1-methyl derivative, 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline, the saponification-product to be expected according to equation I. This substance had, however, been prepared by Fortmann<sup>1</sup> from methylanthranilic acid and phenyl isocyanate, and he gives the melting-point at 233°. In all other respects the body obtained by me and melting at 223° showed the behavior of Fortmann's body. To settle the question, raised by this discrepancy in melting-point, I prepared the same substance by methylating 2-4-diketo-3(N)-phenyltetrahydroquinazoline, in alkaline solution, according to



Two grams of 2-4-diketo-3(N)-phenyltetrahydroquinazoline, dissolved in 65 cc. of methyl alcohol, containing 18 cc.

<sup>1</sup> J. prakt. Chem. [2], 55, 130.



(1 mol.) of  $\frac{N}{2}$ -potassic hydrate was boiled with 5 to 6 grams of methyl iodide for one hour. On cooling, colorless needles separated in considerable quantity. The substance was recrystallized from alcohol containing a little aqueous alkali, to remove any unchanged diketone. After two more crystallizations from pure alcohol, colorless needles, melting at  $224^{\circ}$ , were obtained; neither by further recrystallization from alcohol nor by dissolving in benzene and precipitating with ligroin could the melting-point be raised above  $224^{\circ}$ . An analysis proved the purity of the substance.

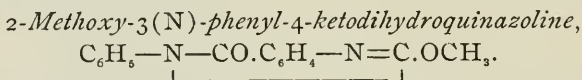
0.2045 gram gave 0.5339 gram  $\text{CO}_2$ , and 0.0866 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_2$ .	Found.
C	71.43	71.22
H	4.76	4.74

The body is therefore 1(N)-methyl-2-4-diketo-3(N)-phenyl-tetrahydroquinazoline. In all particulars, excepting melting-point, it agrees with that of Fortmann. It is insoluble in both acids and alkalies; it has further the exact properties of the methyl body obtained by the saponification of the methylation-product of the body  $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}$ . This was very faintly colored, and melted at  $223^{\circ}$  (instead of  $224^{\circ}$ ), and a mixture with the pure analyzed body melted at  $223^{\circ}$ - $224^{\circ}$ , showing the identity of the two.<sup>1</sup>

To remove the last possible doubt that the body obtained by methylating 2-4-diketo-3(N)-phenyltetrahydroquinazoline in alkaline solution is really the (N)-methyl derivative and not the oxymethyl ether, 2-methoxy-3(N)-phenyl-4-ketodihydroquinazoline,  $\text{C}_6\text{H}_5\text{—N—CO.C}_6\text{H}_4\text{—N=C.OCH}_3$ , this

latter was prepared.

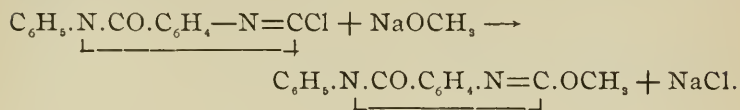


The above oxy-ether was made by heating 2-chlor-3(N)-

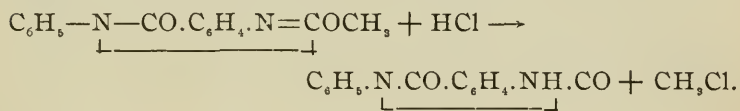
<sup>1</sup> I can assign no reason for the difference of  $9^{\circ}$  between the melting-point of 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline found by Fortmann and that found by myself. As I obtained the substance by two entirely independent methods, I am inclined to think that the lower melting-point, found by me, is the correct one, and that Fortmann's value may be due to a typographical error,  $233^{\circ}$  being given for  $223^{\circ}$ .



phenyl-4-ketodihydroquinazoline with sodium methylate in methyl alcohol, according to



After filtering off the common salt formed and adding a little water, colorless crystals separated, which, after crystallization from methyl alcohol formed, apparently, rhombohedrons melting at  $134^\circ$ . The chloride used melts at  $133^\circ$ , but the new substance contained no chlorine, and a mixture with the chloride showed a strong depression of the melting-point (to about  $110^\circ$ ) as expected. The new body dissolves in concentrated hydrochloric acid and, on warming, a gas which burned with a green-bordered flame (methyl chloride) was given off, while a white insoluble crystalline precipitate was formed. The latter dissolved in dilute alkali, with a blue fluorescence, and was undoubtedly 2-4-diketo-3(N)-phenyltetrahydroquinazoline, formed according to the equation :



The method of synthesis and the behavior with hydrochloric acid leave no doubt that this new ether (m. p.  $134^\circ$ ) is the oxygen ether of 2-4-diketo-3(N)-phenyltetrahydroquinazoline ; the isomeric ether (m. p.  $224^\circ$ ) obtained by methylating the diketone in alkaline solution must therefore be the nitrogen ether, 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NCH}_3\cdot\text{CO}$ , which is in accord

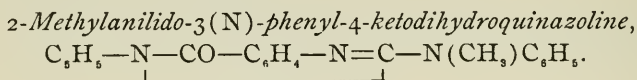
with the behavior of all analogous alkali salts of acid amides when subjected to methylation. The methoxy derivative was not analyzed.

Since 1-(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline, together with aniline, is obtained by the saponification of the methylation-product of the body,  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}$ , as represented by equation I, p. 158, the latter methyl body

(m.p. 174°) must be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline, 
$$\text{C}_6\text{H}_5\text{.N.CO.C}_6\text{H}_4\text{.NCH}_3\text{.C=}$$
  

$$\text{NC}_6\text{H}_5.$$

The above proof of the constitution of the methyl derivative just discussed was fully confirmed by preparing synthetically the only other isomeric methyl derivative that could possibly be obtained by methylating a base of the constitution *a* or *b* (p. 154); *viz.*, 2-methylanilido-3(N)-phenyl-4-ketodihydroquinazoline.

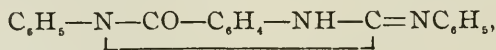


2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline was heated with pure, dry, freshly distilled monomethylaniline to 180° for two hours. The viscous product was treated with hydrochloric acid, in which it dissolved; but very soon a heavy white precipitate, which may have been the hydrochloride of the new base, separated. This was filtered off and dissolved in dilute acid, and precipitated by alkali. By dissolving the free base in methyl alcohol and adding water slowly the body separates in nearly colorless needles, which are very soluble in ethyl and methyl alcohol, less in ether, almost insoluble in low-boiling ligroin, and insoluble in water. The body is a base, being readily soluble in acids and precipitated unchanged by alkalies. For the analysis the body was crystallized from ether by the addition of ligroin, and partial evaporation in a vacuum, and so obtained in colorless needles, melting at 123°.

0.1002 gram gave 11.7 cc. N<sub>2</sub> at 19° and 733.7 mm.

	Calculated for C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O.	Found.
N	12.84	13.24

Not a particle of this low-melting methyl derivative was obtained by treating the white base,

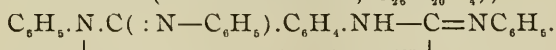


with methyl iodide; the sole methylated derivative was proved to be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetra-

hydroquinazoline (m. p.  $174^{\circ}$ ). If the supposition be correct that, by the action of methyl iodide on the body,  $C_{20}H_{16}N_3O$ , the methyl group has taken the position formerly occupied by the "labile" hydrogen atom, it follows that the body,  $C_{20}H_{16}N_3O$ , has the constitution (a) page 154. Assuming this to be the case, the body has been named accordingly; though as has been pointed out, this assumption is not yet entirely free from objection, and the possibility that (b), page 154, is by no means absolutely excluded.

The preparation of the two isomeric methyl derivatives of the above base,  $C_{20}H_{16}N_3O$ , was carried out with the further object of discovering, if possible, whether the remarkable change of color, when the yellow body,  $C_{26}H_{20}N_4$ , is converted by saponification by acids into the colorless one,  $C_{20}H_{16}N_3O$ , is due to a shifting of the "labile" hydrogen atom giving rise to the isomeric form. The fact that both of the methyl derivatives of the body,  $C_{20}H_{16}N_3O$ , are colorless shows that the isomeric form of the original body, if it could exist, would also be colorless; so that the color of the yellow body,  $C_{26}H_{20}N_4$ , is evidently not due to either possible arrangement of the guanidine group of the molecule. The cause of the color must be intimately connected with the 4-phenylimido group, since when this is removed the body becomes colorless.

*Synthesis of 2-4-Phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline (The Yellow Base,  $C_{26}H_{20}N_4$ ),*



One gram of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline and 0.9 gram of phosphorus pentachloride were dissolved in 5 cc. of phosphorus oxychloride and boiled for ten minutes. No evolution of hydrogen chloride was noted, which was good evidence that chlorination of the benzene rings had not taken place. After distilling off the phosphorus oxychloride the remaining brown oil was mixed directly with about 5 grams of aniline. The reaction took place at once, the mixture became hot, and, on cooling, crystals of aniline hydrochloride separated out. An oil was separated from the crystals by taking up in chloroform and, after removing the solvent, the

oil was boiled for ten minutes with more aniline. On distilling off the aniline, a dark-colored, viscous mass remained. This distilled in a vacuum, with apparently little decomposition, giving a solid yellow distillate, which was dissolved in benzene and the latter partly evaporated. Upon the addition of alcohol a small amount of the characteristic yellow prismatic needles of 2-4-diphenylimido-3(N)-phenyltetrahydroquinazoline ( $C_{26}H_{20}N_4$ ) soon separated out. After recrystallization from alcohol the needles were almost pure and showed the melting-point  $170^{\circ}$ – $171^{\circ}$  (instead of  $171^{\circ}$ ). On cooling, the substance crystallized in the melting-tube, and on reheating melted at  $182^{\circ}$ – $183^{\circ}$  (instead of  $184^{\circ}$ ), showing thus the exact behavior of the yellow body,  $C_{26}H_{20}N_4$ , obtained from carbodiphenylimide.

An addition of the  $\alpha$ -form (prisms, melting-point  $171^{\circ}$ ) of the body obtained from carbodiphenylimide to the substance made synthetically, did not change the melting-point.

It was of great interest to determine, if possible, the cause of the difference between the  $\alpha$ - and  $\beta$ -forms of the yellow body  $C_{26}H_{20}N_4$ . When it was found, from a solution of either of the two forms, that one was obtained which was the less soluble in the solvent used,<sup>1</sup> it was thought that the two forms must be physical or crystallographic modifications of the same substance, and consequently identical in solution, and thus show in solution the same chemical behavior. In endeavoring to determine the position of the hydrogen atom in the yellow bases (*a* and *b*, p. 136) by converting into the urea by means of phenyl isocyanate, and saponifying to the white urea whose constitution has been fairly well established by the methylation process just discussed, the surprising discovery was made that the  $\alpha$ - and  $\beta$ -forms do not seem to act alike in solution. This discovery has been made so recently that the investigation has not been completed, but the point seems so interesting that a brief statement of the facts thus far established will be made now.

*The Action of Phenyl Isocyanate on the Yellow Bases,  $C_{26}H_{20}N_4$ .*

The substances react with great difficulty if cold, and heat-

<sup>1</sup> Vide p. 143.

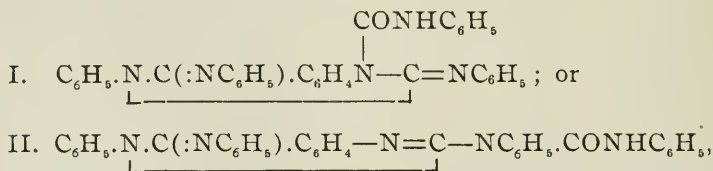
ing is not effective, as was the case in the formation of the urea of the body  $C_{20}H_{15}N_3O$ . To accomplish the reaction I proceeded as follows: 2 grams of the  $\alpha$ -form (m. p.  $171^\circ$ ) of the body,  $C_{26}H_{20}N_4$ , and 1.3 grams of phenyl isocyanate (about double the calculated amount) were dissolved in 100 cc. of pure dry benzene, which was much more than enough to prevent the separation of any of the  $\beta$ -form, and the solution allowed to stand in a well-stoppered bottle, exposed to as much sunlight as possible, for three weeks. At the end of this time the solution remained clear and no crystals had separated. The solution was treated with 1 cc. of alcohol, to destroy the excess of cyanate, and most of the benzene distilled off in a vacuum, the temperature being kept below  $24^\circ$ . The concentrated solution thus obtained gave, with alcohol, a precipitate of perhaps a gram of the nearly pure unchanged body,  $C_{26}H_{20}N_4$ , melting at  $170^\circ$ , instead of  $171^\circ$ . The mother-liquor, on further evaporation in a vacuum at not over  $24^\circ$ , gave a quantity of light-yellow crystals, which melt at  $80^\circ$ – $90^\circ$ , and on heating give off phenyl isocyanate. The crystals so obtained are a mixture of the original base,  $C_{26}H_{20}N_4$ , and the corresponding urea; these were separated by treating with sufficient acetone to dissolve the urea, which is very easily soluble, and leave most of the other body. The acetone solution, on addition of alcohol, gave a crystalline precipitate, which, after dissolving again in acetone and precipitating with alcohol, yielded 0.45 gram of light-yellow diamond-shaped plates. The body, after drying over night in a desiccator, melts at  $80^\circ$ – $90^\circ$  with the evolution of a gas (but no darkening), and by gently heating on a platinum foil gives off much cyanate (recognized by the odor).

A determination of the molecular weight by the freezing-point method in benzene, using 0.43 gram of the substance which had been dried in a vacuum-desiccator over night, gave the value 239 instead of 507, as calculated for the urea,  $C_{33}H_{25}N_5O$ . The low result indicated a dissociation of the urea into two molecules; but that phenyl isocyanate does not split off in the benzene solution is shown by the fact that the urea was recovered unchanged from the above benzene solu-



tion, after partial evaporation of the solvent, by the addition of alcohol, which, if free cyanate had been present, would have united with it forming a urethane. The additional fact, already mentioned, that a gas was given off on melting at  $80^{\circ}$ – $90^{\circ}$ , indicated the presence of some of the solvent, alcohol or acetone, from which the body was crystallized. An experiment seemed to confirm this. A portion of the pure-recovered urea, after drying over night in a vacuum, as before, weighed 0.3664 gram. On keeping in a good vacuum over sulphuric acid, the substance lost weight gradually for a period of ten days, when the weight was 0.3303 gram. The loss amounts to 1.2 molecules of alcohol to one of the urea. The dry urea now melted at  $84^{\circ}$ – $86^{\circ}$  without evolution of a gas.

The larger part of the above urea was lost in an attempted analysis in which the tube broke. That the new body was really the urea was shown, however, by heating 0.05 gram, contained in a test-tube, to  $120^{\circ}$ – $130^{\circ}$  in a bath; much cyanate was given off, and this was removed by a current of air. After a few minutes, when the odor of the cyanate had entirely disappeared, the residue solidified, at the temperature of the bath, to a yellow crystalline mass; this upon dissolving in a mixture of boiling acetone and alcohol and adding a few drops of water crystallized in the characteristic yellow prisms of the  $\alpha$ -form of the body  $C_{26}H_{20}N_4$ . The pure dry crystals so obtained weighed 0.026 gram (theory requires 0.038) and melted at  $171^{\circ}$ ; on cooling, the substance solidified, and on reheating melted at  $184^{\circ}$ . The above crystals (m. p.  $171^{\circ}$ ) mixed with the pure  $\alpha$ -form of the body, showed no change of melting-point. The urea is therefore to be represented by one of the following two formulas:



corresponding to the formulas *a* and *b* (p. 136), respectively,



for the body  $C_{26}H_{20}N_4$ . The ease with which the body decomposes makes it very difficult to carry out any reaction which would discriminate between the two formulas and no solution of the problem has yet been reached.

The  $\beta$ -form of the body,  $C_{26}H_{20}N_4$ , *does not react with phenyl isocyanate*, except to a very slight extent. The experiment was carried out twice in exactly the same manner, and at the same time as that with the  $\alpha$ -form, the same quantity of substance being used. The product treated as before yielded only a very small amount (perhaps 0.05 gram) of a body which was apparently identical with the urea obtained from the  $\alpha$ -form, but the larger part, by far, was the unchanged material.

The difference in behavior towards phenyl isocyanate would seem to show that the two forms of the body,  $C_{26}H_{20}N_4$ , are not identical *in solution*, as would be the case if they were simply physical modifications of the same chemical individual. However, this point cannot yet be considered as settled, and investigation will be continued in this direction.

In conclusion I wish to express my sincere thanks to Dr. Julius Stieglitz, under whose supervision the above investigation has been pursued, for the personal interest he has taken in the work, and for the valuable assistance and instruction received at his hands.

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## ON THE SOLUBILITY OF ARGENTIC BROMIDE AND CHLORIDE IN SOLUTIONS OF SODIC THIOSULPHATE.

BY THEODORE WILLIAM RICHARDS AND HENRY BURNELL FABER.

In the course of a series of experiments having a practical end as their chief aim, several determinations of the solubility of argentic halides in solutions of sodic thiosulphate were made. Since the data concerning this reaction are none too plentiful, it seems worth while to record briefly our incomplete work upon the subject.

The method of procedure was extremely simple. Solutions of sodic thiosulphate of known strength, made by dissolving weighed amounts of pure recrystallized material in water,

were agitated for varying lengths of time in test-tubes at a fixed temperature with an excess of argentic salt. The bromide had been freed from chloride by long continued digestion with potassic bromide, and both argentic halides had been carefully washed, dried, and powdered. At the end of the allotted times, the agitator was stopped, the heavy precipitates were allowed to settle, and two portions were taken from each perfectly clear supernatant liquid by means of an accurate 5.00 cc. pipette. The silver in these portions was now precipitated by sulphuretted hydrogen and collected on a Gooch crucible. Subsequently, the mixed precipitate and asbestos were treated with nitric acid in excess, the nitrous fumes were expelled, and the silver in the mixture was determined by Volhard's method.

The agitator, based upon the apparatus of Noyes,<sup>1</sup> consisted simply of a rotating rod with a number of flat strips of brass soldered at right angles to its axis. The rubber-stoppered test-tubes were strapped to the brass strips by means of rubber bands, and the whole was immersed in a large Ostwald thermostat. A portion of the water of the thermostat was drawn off when it was desired to remove the solutions, so that the mouths of the test-tubes might be uncovered, and of course the projecting mouths were carefully dried. A spring curtain-rod supporter, easily obtained in New England, formed a very convenient support for the rotating rod, when soldered to the sides of the thermostat. The results with the second solution showed that four hours' agitation was enough to insure saturation. No claim of great accuracy is made for the figures; indeed, the variations among them show their crudity; but they more than sufficed for our purpose, and are trustworthy enough to form an adequate basis for the remarks which follow.

<sup>1</sup> Ztschr. phys. Chem., 9, 606; also Schröder: *Ibid.*, 11, 454.

*The Solubility of Argentic Bromide in Solutions of Sodid Thio-  
sulphate.*

Temperature = 35°.

	Cryst. sodic thiosulphate in liter. Grams.	Weight of sil- ver found in 5.00 cc. solution. Gram.	Time of agitation.	Weight of AgBr cor- responding to each gram of thiosulphate. Gram.	AgBr corre- sponding to Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Molecule.
1	100	0.110	4 hours	0.376	0.496
2		0.108			
3		0.106			
4		0.109			
		0.108			
5	200	0.228	4 hours	0.390	0.515
6		0.224			
7		0.225			
8		0.225			
9		0.226	16 hours		
10		0.223			
11		0.220			
12		0.223			
		0.224			
13	300	0.339	4 hours	0.397	0.524
14		0.340			
15		0.347			
16		0.341			
17		0.344			
18		0.337			
19		0.337			
		0.341			
20	500	0.613	4 hours	0.427	0.564
21		0.611			
22		0.611			
23		0.619			
		0.613			

It is thus evident that the quantity of argentic bromide increases more rapidly than the quantity of the thiosulphate. In this respect the behavior of the bromide resembles that of

the chloride, as observed by Stetefeldt<sup>1</sup>. Hence, simply judging from the solubility, one has a right to infer that the solubility concerns itself with the undissociated part of the sodic salt, for this is the part whose proportion increases when the concentration is increased.

The nature of the equilibrium is obviously so complex that the molecular ratios could not be expected to consist of simple whole numbers. Neither could the solubilities of the two halides be expected to conform to one another. In order to test this point, the solubility of argentic chloride in a solution of sodic thiosulphate containing 200 grams of the crystallized salt to the liter was determined. Four parallel analyses of 5.00 cc. of the solution saturated at 35° yielded respectively 0.344, 0.341, 0.342, and 0.341 gram of silver, or on the average, 0.454 gram of argentic chloride per gram of sodic thiosulphate.<sup>2</sup> Thus the molecular ratio was in this case 1 : 0.78 instead of 1 : 0.52 as in the case of the bromide. The difference is undoubtedly due to the different solubilities of the argentic halides in water, which of course must be factors in the complex equilibrium.

It is well known that from these solutions two well-marked double salts<sup>3</sup> (or, more probably, complex salts) may be obtained by crystallization; but of course this fact does not show that these salts exist in the solution. As Barth has pointed out,<sup>4</sup> however, the inability of the solution to give the ordinary reactions of silver shows that a complex ion must be formed. More light might obviously be obtained from observations on the freezing- and boiling-points, as well as of electrolytic conductivities: indeed Barth made an interesting beginning in this direction, and obtained evidence of the existence of a trivalent acid ion in the solution.

We proceeded in a somewhat different manner:—instead of studying the behavior of the pure double salt, we observed

<sup>1</sup> C. A. Stetefeldt. *The Lixiviation of Silver Ores*: (Craz and Gerlach, Freiberg, Saxony).

<sup>2</sup> Russell found 0.400 and 0.485 by two different methods. The first was evidently not saturated, the second supersaturated. Stetefeldt, p. 19, 20.

<sup>3</sup> Herschel: *Edinb. Phil. Jour.*, 1, 26 and 398, (1819). Also Lenz: *Ann. Chem. (Liebig)*, 40, 94 (1841).

<sup>4</sup> Barth: *Ztschr. phys. Chem.*, 9, 217, (1892).

the change in the freezing-point caused by the addition of argentic bromide to solutions of sodic thiosulphate. In one trial, the addition of 0.8 gram of argentic bromide to 26 grams of a 0.54 mole-solution<sup>1</sup> of sodic thiosulphate *raised* its freezing-point  $0.08^{\circ}$ , while in another trial the addition of 0.25 gram of argentic bromide to 19 grams of a 0.4 mole-solution raised its freezing-point  $0.03^{\circ}$ . Further additions in both cases produced no further rise, although much more argentic bromide dissolved; indeed, in the first case a slight fall was subsequently observed.

According to modern hypotheses such a rise in the freezing point can be produced only by the diminution of the number of active particles present. In the present case the addition of another salt with different ions must, as usual, increase rather than diminish the dissociation of the sodic thiosulphate molecule, hence it could have diminished the number of active particles only by causing some of the undissociated material to condense into a complex structure, in which the silver is combined. Thus further evidence of the plausibility of Barth's conclusion as to the existence of a complex ion is afforded. The fact that upon the further addition of argentic bromide, no further rise is produced may be accounted for by the possible concomitant formation of another complex group, containing more silver—a reaction which might involve an increase in the number of active particles. The substances corresponding to these stages may well be the salts  $\text{Ag}_2\text{S}_2\text{O}_3$ ,  $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and  $2\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , which are actually known in the solid state. The double formula is assigned to the second salt, simply in order to show, at a glance, that it contains more silver than the first. It is more likely that this second salt possesses a simpler formula, and that its partial formation, even in the beginning, prevents the rise in the freezing-point from being as great as it would be if influenced by the formation of ions of the first salt alone.

In the course of the work, the depression of the freezing-

<sup>1</sup> That is, a solution containing  $0.54 \times 248.3$  grams of sodic thiosulphate in a liter. Such a solution would be called by some a 0.54 normal solution; but it seems to us that this nomenclature is an unfortunate one, and that the term "normal solution" should be reserved for the *equivalent* solutions so useful in volumetric analysis.

point of water caused by the addition of sodic thiosulphate was also observed, as follows :

g. mol. in liter.	Depression of freezing-point.
0.202	0.855°
0.404	1.590°
0.535	1.980°

In brief, this paper contains data concerning the solubility of argentic bromide and chloride in solutions of sodic thiosulphate, cognate results upon the freezing-points of the solutions, and a few remarks upon the probable nature of the complex substances formed. The subject is one of great interest, but the time at our disposal, as well as the inherent obscurity of the equilibria of concentrated mixed solutions, does not suffice to present a more complete view of the details of the reaction.

CAMBRIDGE, MASS., NOVEMBER 26, 1898.

## • NOTE ON THE SPECTRA OF HYDROGEN.

BY THEODORE W. RICHARDS.

In a recent paper B. S. Hutton recounts some interesting experiments, which tend to show that Hasselberg's "white spectrum" of hydrogen really belongs to that substance, and not to impurities<sup>1</sup>. One point he was unable wholly to explain—the fact that Cornu<sup>2</sup> and he always obtained a brilliant red four-line spectrum of hydrogen whenever a trace of oxygen was present. The experience recently gained by Professor Trowbridge and the writer upon this subject furnishes the data for an explanation of the matter, and the object of these few words is to remove the uncertainty<sup>3</sup>.

We observed that water vapor under diminished pressure gives the pure red spectrum far more readily than hydrogen itself does, and that when aqueous vapor is mixed with elementary gases it seems usually to be the chosen vehicle for the transport of the electricity. Obviously water must have been formed in Hutton's and Cornu's tubes, and this must have been the source of the red spectrum. The fact that

<sup>1</sup> Hutton : *Phil. Mag.*, September, 1898, p. 338.

<sup>2</sup> Cornu : *Journ. de Phys.*, [2] 5, 100-103 and 341-354, (1886).

<sup>3</sup> *Am. J. Sci.*, 3, 117 and 327, or *Phil. Mag.*, [5] 43, 135 and 349, (1897).



water vapor thus conducts electricity easily may be accounted for by its heterogeneous molecular constitution<sup>1</sup>, which is naturally more sensitive to electric stress than the homogeneous structure of the hydrogen molecule. This is only one of the many arguments which go to support the hypothesis that the red spectrum of hydrogen is due to dissociated atoms,—or at any rate to the disturbance caused by the act of dissociation, while the white spectrum is due to a compound structure of polarized particles. Obviously from water only the characteristic lines of atomic hydrogen, not those of molecular hydrogen, could be obtained : and these are obtained so easily that the molecular spectrum of water steps into the background. On the other hand, if the hydrogen is quite dry, as was evidently the case in some of Hutton's as well as in our experiments, the red spectrum requires tremendous heat for its appearance in a state of purity,—a circumstance which hypothesis explains simply by ascribing great stability to the polarized molecular structure of the gas.

Randall has recently published a paper in which he recounts his difficulties in obtaining the pure hot red spectrum of hydrogen free from relics of the cool white one.<sup>2</sup> Strangely enough he speaks of the presence of aqueous vapor as a possible cause of the existence of the white spectrum, when experimentation would have shown him that the absence of water alone makes this spectrum possible in a state of purity. He seems to have overlooked the fact that a large capacity (10,000 electrostatic units, or more according to circumstances) charged with a very high electromotive force—in other words, great current strength—is necessary in order to provide enough heat to yield the hot spectrum from dry hydrogen, even at its tension of least resistance. This tension varies from one-half to one millimeter of mercury, according to the current strength, a value in any case lower than the tensions employed by him (3 to 8 mm.). It is very certain that an ordinary Ruhmkorff coil and Leyden jar, such as those used by Randall, could not yield the red spectrum under

<sup>1</sup> Compare Volterra : *Ztschr. phys. Chem.*, **27**, 375. (1898); also J. Zeleny : *Phil. Mag.* [5] **46**, 120-154. (1898) etc.

<sup>2</sup> W. W. Randall : *This JOURNAL*, **19**, 682, (1897).

his circumstances, provided that the gas was dry, as his seems to have been.

It is odd that Randall, while commenting upon a supposed absence of data in our papers concerning the source of our hydrogen, should have himself forgotten to state his mode of generating the gas. His drying train seems to have included sulphuric acid, a dangerous absorbent of water where hydrogen is concerned, but this could not have effected the final result, for the gas whose spectrum he observed had been diffused through platinum. Our hydrogen was prepared by electrolysis from pure dilute hydrochloric acid, was freed from acid by large amounts of potash, and was dried by standing over phosphoric oxide<sup>1</sup>. It is needless to say that we took all the necessary precautions about sweeping out and filling the tubes, so well known to anyone who has had experience in observing the spectra of gases. One regrets that Randall should have fancied a disagreement between his results and ours, when in reality they are wholly concordant.

In the light of all the facts, and the obvious explanation of Cornu's apparent discrepancy, one can hardly doubt that Hutton and others are quite right in ascribing to hydrogen itself, and not to impurity, the "cool" white spectrum of many lines.

CHEMICAL LABORATORY OF HARVARD COLLEGE, DECEMBER 7, 1893.

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## REPORT.

### ON AQUEOUS SOLUTIONS OF METALLIC GOLD, AND ON THE PURPLE OF CASSIUS.

In a recent number of the *Annalen der Chemie*<sup>2</sup> Richard Zsigmondy has published an interesting account of soluble metallic gold, obtained by reducing gold chloride in very dilute aqueous solution. The following is an abstract of his paper :

Gold can be held in solution in water in different colored conditions. Although the great variety of colors obtained from the colloidal silver of M. Carey Lea cannot be obtained with gold, yet gold solutions are obtained which are deep-red, blue, and black, as well as of shades lying between these col-

<sup>1</sup> Compare *Am. J. Sci.*, **3**, 331; a paper published three months before the date of Randall's. Hutton also overlooked this paper.

<sup>2</sup> *Ann. Chem. (Liebig)*, **301**, 29.

ors, according to the conditions under which the gold is reduced. The blue or violet solutions seem to be the most easily obtained. The red gold solution is the one principally studied. It is obtained by treating very dilute, boiling-hot, and slightly alkaline solutions of gold chloride with different reducing agents, such as formic aldehyde, acetic aldehyde, alcohol, or even hydroxylamine. Many attempts were made, with varying success, but the best conditions are the following: 25 cc. of a solution of chlorauric acid,  $\text{AuCl}_3 \cdot \text{HCl}$ , containing 0.6 gram to the liter, diluted with 100 to 150 cc. of pure distilled water, and rendered alkaline by the addition of 2 to 4 cc. of a  $\frac{2}{10}$ -normal solution of potassium carbonate, are heated to boiling. As soon as the liquid begins to boil, it is removed from the flame, and 4 cc. of a solution of 1 part of freshly distilled formic aldehyde in 100 parts of water, is added gradually to the boiling-hot gold solution. In a short time the colorless liquid darkens, becomes light red, and in a few seconds attains a deep-red color, which does not change in the slightest degree on boiling or on standing for months.

If the above directions are not strictly adhered to, not clear red, but darker purple and often violet and blue-black, turbid liquids are formed. The very dilute red solution can be evaporated to half its volume without change, but further boiling will cause it to change to a dark-violet color, and gold will be precipitated as a black powder. The precipitation is probably due to the accumulation of salts which tend to precipitate the dissolved colloidal gold. The solution was purified by dialysis at a temperature of  $40^\circ$  to  $50^\circ$ . The solution can thus be reduced to one-twentieth of its volume in a few days, and solutions containing 0.12 per cent. colloidal gold were obtained, but on further concentration metallic gold was precipitated on the parchment.

The red gold solution passes through the closest filter-paper without change. It is tasteless. On addition of neutral salts, acids, or fixed alkalies, the beautiful red color changes to blue; the liquid becomes turbid, gradually losing its color, and in eight or nine hours the gold all falls to the bottom as a blue-black powder. Potassium ferrocyanide seems to act differently from other salts; it changes the color to green, and after twenty-eight hours to pure yellow, but the gold is not precipitated. Ammonia changes neither the color nor the solubility of the gold. The addition of an excess of alcohol changes the color to dark-violet and precipitates the gold

completely, but the precipitate, at times, retains its solubility in water.

The metallic gold in aqueous solution acts just as most other dissolved colloidal substances when subjected to electrolysis, following the negative electricity to the positive pole, where it is deposited as a black powder, which can readily be recognized as metallic gold when allowed to dry, as it immediately assumes a beautiful golden luster. When a membrane is placed between the electrodes, the gold, like a true colloid, does not pass through the membrane, but is deposited upon it on the negative side.

Mercury does not amalgamate with dissolved gold either on being agitated with the solution or on boiling, and even when precipitated with salts amalgamation takes place very slowly and incompletely.

That the dissolved body is really metallic gold and not aurous oxide is shown by analysis of the precipitate caused by sodium chloride. The very small volume of oxygen found is undoubtedly due to air condensed on the surface of the very finely divided precipitate while drying, especially as the equivalent volume of nitrogen was also found.

When we consider the results of analysis together with the fact that gold with metallic luster is deposited on slow evaporation, and further that the reduction was carried out in a boiling-hot solution and by means of a strong reducing agent there can be no doubt that the red solution contains gold in the metallic condition.

The similarity between the colors of these solutions of gold and the colors of thin layers of gold by transmitted light is marked as well as that of red and rose ruby glass. The absorption spectra of the red solution compared with ruby glass, of the blue and violet solution with blue and violet colors of thin layers of metallic gold by transmitted light are almost identical.

In an appendix to his paper the author referred to the fact that Faraday, in a paper on the "Experimental Relation of Gold to Light<sup>1</sup>," described many of these phenomena and actually obtained the red solution of gold but did not recognize it as such, attributing the color to suspended gold in a finely divided condition.

In the same number of the *Annalen*<sup>2</sup> Zsigmondy has published another article on "The Chemical Nature of the Purple of Cassius," in which the nature of this curious substance seems finally to be cleared up.

There are few substances in the field of inorganic chemistry

<sup>1</sup> Phil. Trans., 1857, 145.

<sup>2</sup> Ann. Chem. (Liebig), 301, 361.

on which so much has been done, and so much written with as little result as this purple of Cassius. Up to the present time there have been two views held as to the chemical nature of this substance; the one that it is a mixture of stannic acid, and metallic gold; and the other, that of Berzelius, that it is substantially a chemical compound of purple gold oxide with the oxides of tin, possibly mixed with an excess of stannic acid.

The solubility of the substance in ammonia favors the latter view, although Schneider lays great stress on its colloidal character and considers the ammoniacal solution as a mixture of the "hydrosols" of gold and stannic acid.

It seemed very likely that the substance is a chemical compound of acid character, and that the solubility in ammonia is due to the formation of a salt, but it was found that by oxidation of stannous chloride, and by allowing very dilute solutions of stannic chloride to stand, the "hydrogel" of stannic acid separated out, which on the addition of a few drops of ammonia liquefied, and so became soluble in water, just as the purple of Cassius does. There can therefore be no salt formation here.

After the solutions of metallic gold in water were obtained, a substance in every way identical with the purple of Cassius was made by mixing colloidal stannic acid with colloidal gold, and precipitating with acids.

The paper is divided into three parts, the first of which is devoted to showing that the substance is not of acid character in its relation to ammonia, and to the preparation of colloidal stannic acids. This part of the work was done with J. Robitschek.

The purple of Cassius was prepared according to the method of Golfier Besseyre,<sup>1</sup> from stannous chloride solution, free from stannic chloride, and gold chloride. The washed and dried preparation was soluble neither in ammonia nor in caustic potash, but when moistened with hydrochloric acid, it was easily soluble in water. When fresh and moist it is insoluble in concentrated ammonia, potassium hydroxide, or potassium carbonate, but dissolves on dilution. The ammonia solution can be boiled if left dilute so that no odor of ammonia can be detected even on addition of caustic potash, and only a trace can be detected by titration, without precipitating the substance. That the solubility in ammonia or potassium hydroxide is not due to the formation of a salt is also shown by the small percentage of these substances found on analysis—0.003 ammonia in 1 gram and 0.4 cc. normal alkali in 1

<sup>1</sup> Ann. chim. phys., 54, 40.



gram. The solubility in these reagents seems to be due to the liquefying property of the alkalies. The purple of Cassius behaves in every way like a colloid substance toward the electric current and porous membranes.

By passing a strong current of air through a very dilute solution of stannous chloride, free from gold, and allowing it to stand, it was oxidized gradually to a colloid stannic acid, which is precipitated, and, when washed free from chlorine, behaves toward reagents neither like ortho- nor meta-stannic acid. It is insoluble in strong hydrochloric acid, nitric acid, or caustic potash, but dissolves immediately on diluting to double the volume. It is soluble in water after moistening with ammonia. We have here the "hydrogel" of stannic acid which behaves toward the electric current like the purple of Cassius.

A colloidal stannic acid can also be obtained from stannic chloride when a very dilute solution of the latter (2 grams in 3 liters) is allowed to stand for several hours. A voluminous precipitate comes down which, when washed free from chlorine, moistened with a few drops of ammonia, and diluted, dissolves to a clear liquid which can be boiled without precipitation of stannic acid. This preparation differs from the former in that it is soluble in strong or dilute hydrochloric acid, and potassium hydroxide, and not entirely in nitric acid. Potassium carbonate precipitates it from its hydrochloric acid solution but does not dissolve it in excess.

From their properties these forms of stannic acid are seen to be neither ortho- nor meta-stannic acid, but they can be looked upon as colloidal mixtures of the two rather than individuals lying between the two, the properties of the one being hidden by those of the other. The purple of Cassius is such a mixture of gold and stannic acid hydrate, in which the stannic acid imparts to the metallic gold the property of dissolving in water by means of alkalies. This is the reason why so many chemists have for so long a time considered the substance to be a chemical compound. By mixing a solution of either of these colloidal stannic acids with a solution of colloidal gold, and precipitating by means of dilute acids or salt solutions, a gold-purple can be obtained of any desired composition and intensity of color, in fact any of a great variety of shades. The mixture does not turn blue and then precipitate gold when treated with acids or salts, like the red gold solution, but remains unchanged even on long standing, but when boiled a red body is precipitated which behaves, in every respect, like the purple of Cassius.

The formation of the purple of Cassius is explained by



assuming that when stannous chloride is added to a sufficiently dilute solution of gold chloride, the latter is immediately reduced to metallic gold, while stannic chloride is formed. Generally after a few seconds the liquid becomes red, but the purple is not precipitated for several days unless it is heated. The gold is not precipitated as a black powder because the stannic chloride formed is immediately hydrolyzed into hydrochloric acid and the hydrate of stannic acid. The latter prevents the aggregation of the gold particles, and the stannic acid remains in solution as a colloid which on standing gradually changes under the influence of the dilute hydrochloric acid to an insoluble form, the "hydrogel" of stannic acid. By heating, this change takes place immediately.

The properties of purple of Cassius depend on the properties and character of the stannic acid present, the gold playing a passive rôle in its relation to reagents. If the stannic acid is soluble in concentrated hydrochloric acid, so is the purple, but if it has the properties of metastannic acid, it is insoluble in that reagent but dissolves on distillation. In the same way the solubility in ammonia or dilute alkalis depends upon the character of the stannic acid present; in fact the great variety in the properties of the stannic acids explains the many contradictions in the literature with reference to the properties of the purple of Cassius. Zsigmondy says, "I look upon the knowledge that a mixture of colloid bodies can behave under some conditions as a chemical compound, and that the properties of one body in such mixtures can be hidden by those of another, as the most important conclusion to be drawn from this work."

By mixing the "hydrogels" of stannic acid and silver and precipitating with dilute sulphuric acid, a red-yellow body was obtained, which is soluble in ammonia, and a similar body was also obtained by reducing silver nitrate in the presence of a stannic acid solution.

C. L. REESE.

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## REVIEWS.

TRAITÉ D'ANALYSE DES SUBSTANCES MINÉRALES. Par ADOLPHE CARNOT. Tome premier; Méthodes générales d'Analyse qualitative et quantitative. Paris. V<sup>e</sup>e Ch. Dunod. 1898. 992 pp.

This, the first of three volumes, gives promise of one of the most extensive and important works on inorganic analysis which have appeared for very many years, and well fulfils the promise as far as general methods are concerned, leaving to the remaining two volumes, soon to be completed, the detailed and special methods applicable to particular classes of material. The whole work is to contain about 3000 pages.

In the volume already published the first chapter is devoted to the use of the blowpipe, the second to Bunsen's flame reactions, and the third to the spectroscope, this last giving much fuller information as to the use of the instrument, particularly with the aid of high temperature electric sparks, than is found in most of the common manuals of chemical analysis. In the fourth chapter much useful information as to characteristic reactions observable under the microscope—so-called micro-chemistry—has been brought together from sundry separate works and individual memoirs. The fifth chapter takes up the means of getting into solution substances to be examined, and the group reactions in the liquid way of the solutions obtained; in this the rare elements, such as thallium, germanium, indium, and thorium, are treated of on the same footing as the most common. The sixth chapter is devoted to the individual reactions of the several basic and acid radicals, given in much detail—thus, under manganese we have separate consideration of manganous and manganic salts, of manganates and permanganates, and under sulphur we have sulphates, sulphites, thiosulphates, sulphides, hydrosulphites, di-, tri-, tetra-, and pentathionates. Chapter VII discusses reagents, gives directions for obtaining these in a pure state, including such substances as hydrogen and oxygen gases, and takes notice of some recently introduced or less common reagents, such as sodium dioxide, ammonium formate, calcium thiosulphate, and bismuth chloride. In chapter VIII quantitative analysis is begun, and the selection and purification of samples, pulverization, desiccation (under various conditions), and weighing are considered. Chapter IX contains the details of operations in the dry way at high temperatures, with good descriptions of furnaces (for solid and gaseous fuel), crucibles, etc., and useful information as to calcination, fusion, etc., which reflects in part the experience of the author as professor of assaying in the *École des mines* at Paris. In Chapter X we have a discussion of the chief apparatus and processes used in operations in the liquid way—solution, evaporation, distillation, filtration, etc. Chapter XI is devoted to modern electrolytic apparatus and methods, of which a clear general account is given, including the measurement of currents—special applications of electrolysis are reserved for the succeeding volumes. Volumetric methods, the measuring vessels, choice and preparation of standard solutions, indicators, etc., are treated of in Chapter XII—individual determinations are left over to the later volumes. In Chapter XIII there is a rather brief account of colorimetric methods, less full and satisfactory, perhaps, than any other part of the

book. The fourteenth and last chapter is taken up with the means of analyzing gaseous mixtures, the collection of samples of gas from mineral springs, the soil, furnaces, chimneys, and other sources, and the apparatus and processes of gas analysis, with notice of the methods for detecting and quantitatively determining fire-damp in the atmosphere of coal mines.

The large volume is well printed, and well illustrated, and amply deserves a place on the book shelves of every well-equipped laboratory.

J. W. M.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York. The Macmillan Company. 1898. xvii + 541 pp.

This book is intended, as the author says in his preface, to furnish an elementary course for students in Industrial Chemistry, which may serve as the groundwork for a more extended course of lectures, if desired. It seems to carry out this purpose in a way likely to be useful.

In the treatment of so extensive a subject scarcely any two teachers, perhaps, would agree exactly as to what should be included and what omitted, or as to the relative amount of space to be devoted to the various subdivisions of the work. Metallurgy is altogether left out, as representing an independent branch of study, and the whole subject of artificial dye-stuffs is treated in nine pages. Some may be inclined to think that at least a little space might have been given to such matters as bread-making, milk and its manufactured products, artificial stone, the preservation of timber, and the new industry of synthetically made materials for use in perfumery. And perhaps enumeration of the different inks now in use might more advantageously have taken the place of mention given to such materials as assafœtida, euphorbium, myrrh, and Iceland moss. But on the whole the distribution of matter is good, and the condensation has been judiciously effected.

The point which seems to the writer of this notice most open to criticism is meagreness in the description, and lack of the necessary wood-cuts, to render intelligible machinery and appliances for the actual conduct of several important processes, such as the manufacture of gunpowder, calico-printing, etc. Nothing should more markedly distinguish the teaching of industrial from that of general or scientific chemistry than a clear discussion, not only of what result is aimed at in each manufacturing process, but further of just *how* such result is practically reached with most economy of material, labor, and time. In this direction the author of the book un-

der review has done well to begin with a chapter on some of the most common and variously applied processes, such as lixiviation, evaporation, etc. But this chapter might well have been expanded, so as to include, for instance, a notice of *systematic* leaching in order to separate soluble from insoluble material with maximum completeness and minimum quantity of the solvent, and a fuller explanation of the purification of substances by crystallization from solution, washing of the crystals, disposal of mother-liquors, etc. More than merely incidental reference might well have been made to the electric furnace and its increasing use, and to the growing extension of electrolytic processes. It is always desirable to draw the attention of students to analogous or competing methods of reaching the same ends, and to present clearly the advantages and drawbacks which severally belong to them—thus, for example, it is very instructive to contrast fully the Leblanc with the Solvay process for making carbonate of soda, and the conditions under which gunpowder and the modern “high explosives” may respectively replace each other with advantage in use. Such comparisons are not altogether neglected in this book, but they might perhaps have been made more prominent. A very good feature of the work is the list, given at the end of each chapter, of references to more extended works, papers in scientific journals, etc., where the student may find fuller details when desiring to go further into the subject and to specialize his knowledge of it.

The general impression made by the book is decidedly favorable, and it is to be hoped that it may meet with such success as to cause a demand for other editions, in which it may be rounded out by improvement in some details, and may become a standard text-book. There has been much need for such a work in English, v. Wagner’s well-known *Handbuch der chemischen Technologie* being deformed by absurd blunders of translation—such as the confusion of geographical degrees of latitude with degrees of the thermometric scale!—blunders which have been perpetrated in an earlier and perpetuated in the last edition.

J. W. M.

A SHORT MANUAL OF ANALYTICAL CHEMISTRY, QUALITATIVE AND QUANTITATIVE—INORGANIC AND ORGANIC. By JOHN MUTER. 2d American, adapted from the 8th British edition. Philadelphia: P. Blakiston’s Son & Co. 1898. xiii+228 pp.

This manual proposes to give a concise course of instruction in chemical analysis, qualitative, quantitative, and in special applications, primarily and chiefly for students of pharmacy. The condensation of matter is certainly remarkable, and its selection has no doubt been on the whole judiciously made in



the interest of those for whom the book is intended. They will find much information of a practically useful sort in such chapters as that on the detection of alkaloids (including some of the less familiar members of this class, as narceine, physostigmine, pilocarpine, etc., and with them some substances not alkaloidal in character, but liable to be confounded with alkaloids, as acetanilid and antipyrin), that on the detection of some miscellaneous organic substances interesting in connection with medicine or pharmacy—*e.g.*, benzine (petroleum spirit), and benzene from coal-tar, beech-tar creosote, paraldehyde, naphthol, resorcin, phenacetin, sulphonol, etc.,—that on the analytical examination of important drugs (assay of opium and of cinchona bark, detection of “methylated spirit” in tinctures, etc., examination of fixed oils and fats, of soaps, and of so-called essential oils, etc.).

But it may well be doubted whether condensation has not been carried too far. The book is manifestly intended for practical use in the laboratory, and one cannot but hesitate as to the safety with which important investigations may be based on such instructions as can be given within some of the limits observed. Thus, the “general sketch of the method of testing for poisons in mixtures” takes up less than a page and a half, the individual reactions, it is true, being given elsewhere. The use of the polariscope is disposed of in two pages, and spectrum analysis in little more than a single page.

While a very large amount of information has been included, there are here and there noticeable omissions of statements that one might naturally expect to find. For example, in describing the reactions of cobalt no mention is made of the well-known yellow cobalt-potassium nitrite, and for the detection of nitrites no reference is made to the Griess reaction with sulphanilic acid and a salt of naphthylamine. Neither in the description of the reactions of arsenic nor in the chapter on poisons is any hint given, in connection with Marsh’s and Reinsch’s tests, of the need for care as to the freedom from arsenic of the reagents used.

The book is to some extent marred by occasional loose forms of expression, a defect which is much to be deprecated when the mental interests of students are considered. Thus, on p. 1, “Solution” is defined in these words—“This process consists in leaving a *solid* body in contact with a fluid until it dissolves, heat being occasionally used.” Aside from the objection to defining the noun by the same word in the form of a verb, there is here no recognition of solution affecting a gas or a second liquid. Again, on p. 2, “Precipitation” is defined—“This process consists in mixing the solutions of two

substances *so as to form a third substance*, which, being insoluble in the fluids employed, sinks to the bottom." The common pharmaceutical process of precipitating an alcoholic solution of camphor by addition of water does not involve the formation of a third substance. On p. 5, the expression is used—"A *peculiar kind of fusion*, called cupellation, is resorted to in the assay of gold and silver bullion." This is hardly a satisfactory definition of cupellation. On the same page, in explaining what is meant by crystallization, it is stated that "Many substances when dissolved in a boiling liquid separate out, *as soon as the fluid cools*, in masses having a well-defined and symmetrical shape." This does not apply to the case of common salt crystallized by evaporation of water from continuously heated brine, and a beginner without experience might easily derive the idea that when a heated (why boiling?) solution cools the *whole* of the dissolved solid separates in crystallized form. There is no mention of substances like iodine or benzoic acid, crystallized on condensation of the vapor. On p. 96, in illustration of the mode of using the hydrometer it is said—"Suppose an elongated body with a weight at its base to cause it to float upright, which has a specific weight exactly half that of water, be immersed in that fluid, it will sink to exactly half *its length*." This certainly is not true of a hydrometer of the usual form, such as is shown by a wood-cut on the next page, nor is it true even of a cylinder or prism of uniform cross-section having "a weight at its base." On page 100 we have the following decidedly unscientific problem and general solution thereof—"To find the amount of solid matter" (No particular kind of matter is referred to, nor is the solvent specified; presumably water is meant), "in grammes, present in 100 cc. of a solution of a given specific gravity. So far as any ordinary rule" (What is an ordinary rule?) "can be laid down, especially with regard to saccharine liquids, for which this calculation is generally used, we multiply the gravity by 1000, and then, having deducted 1000 from the product, we divide by 3.85." On p. 104—"Volumetric or standard solution is a solution of definite strength, made by dissolving a given weight of a reagent in grams in a definite volume *of water* in cubic centimeters." In all the standard solutions commonly used in volumetric analysis, such as are referred to in the following pages, the "definite volume" required is not that of the water, but of the solution. In quoting these examples, italics, not those of the author, have been made to indicate the words unfortunately used.

J. W. M.



# AMERICAN CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

## LXVIII.—ON THE REARRANGEMENT OF IMIDO-ESTERS.

BY H. L. WHEELER AND T. B. JOHNSON.

The fact that the silver salts of the amides give imido-esters with alkyl halides was observed simultaneously, in the year 1890, by Tafel and Enoch<sup>1</sup> and by Comstock.<sup>2</sup> As we had occasion to prepare ethyl phenylimidoformate,  $\text{HC} \begin{array}{l} \nearrow \text{NC}_6\text{H}_5 \\ \searrow \text{OC}_2\text{H}_5 \end{array}$ ,

by their method, and, wishing to avoid the slow process of warming silver formanilide suspended in ether with ethyl iodide for several days, we heated a portion of the silver salt to 100° in a closed tube with an excess of ethyl iodide. An oil was thus obtained which did not contain a trace of the expected imido-ester. The entire reaction-product was *N*-ethyl-

formanilide,  $\text{H}-\text{C} \begin{array}{l} \nearrow \text{N} \begin{array}{l} \nearrow \text{C}_6\text{H}_5 \\ \searrow \text{C}_2\text{H}_5 \end{array} \\ \searrow \text{O} \end{array}$ .

In order to assure ourselves that our material was not at fault, we boiled another portion of the same sample of silver salt, in an open vessel, with an ether solution of ethyl iodide and got an excellent yield of the sought-for, isomeric, imido-ester.

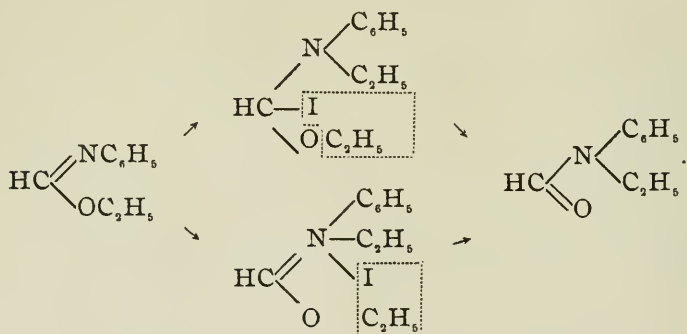
<sup>1</sup> Ber. d. chem. Ges., 23, 103 and 1550.

<sup>2</sup> *Ibid.*, 23, 2274 and R. 659; also This JOURNAL, 13, 514.

This "tautomeric" reaction of the silver salt with ethyl iodide is remarkable since the difference of conditions in the two cases cited is so small—a difference of temperature less than  $65^{\circ}$  and only slight increase in pressure in the case of the reaction in the closed tube.<sup>1</sup>

Another portion of the same salt was heated again in a closed tube to  $100^{\circ}$ , as in the previous experiment, except that in this case a little less than the calculated amount of ethyl iodide was used, when little or no imido-ester was obtained.

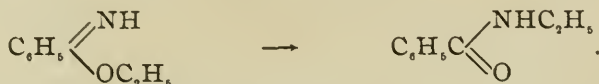
These facts suggested that in the case of the reactions in the closed tube we have not a single reaction but a set of reactions. The first and intermediate product, the imido-ester, under the conditions of the experiment, reacts further with the ethyl iodide to give *N*-ethylformanilide. This must take place by addition in either of the following two ways :



That is, ethyl iodide is either added to the carbon and nitrogen that are doubly linked together, or entirely to the nitrogen, and then separates again in another manner as indicated by the dotted lines.

<sup>1</sup> These striking results show that the method of preparation of a compound proves nothing in regard to its structure and that arguments concerning structure, based solely on the compounds formed in a reaction, have no weight. In the sodium salts of the amides the metal is universally represented as attached to nitrogen simply because these salts give nitrogen alkyl compounds with alkyl halides. That the metal is attached to nitrogen in these compounds is improbable. The above reactions show that slight changes in conditions may produce opposite results, and the difference in conditions when alkyl halides act on sodium salts on the one hand and on silver salts on the other, is certainly great—greater at least than is necessary to produce the opposite results in the case of the same material, *i. e.*, the silver salts.

That this is the course of the reaction is shown by the fact that benzimidooethylester, prepared by Pinner's method from benzonitril, when heated with ethyl iodide at  $100^{\circ}$ , gives practically nothing but ethylbenzamide :



The reaction taking place as shown above has the effect of simply transferring the ethyl from its union with oxygen to the nitrogen.

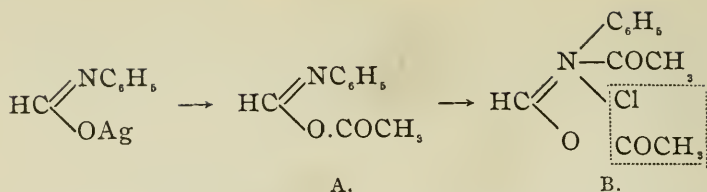
The tautomeric reaction in these cases, as in others, is undoubtedly nothing but a reaction by addition.

The above cases are the first that have been observed where a silver salt of an acyclic amide, anilide, or imido-ester give nitrogen derivatives with alkyl iodides.<sup>1</sup> The behavior of the silver salts and imido-esters with alkyl halides under pressure and at a somewhat elevated temperature is analogous to their behavior with acyl chlorides in the cold. It was shown in previous papers,<sup>2</sup> on the compounds in question that the silver and mercury salts of the anilides, and the corresponding imido-esters give the same diacylanilides, and that nitrogen-substituted derivatives resulted in each case.

The above action of ethyl iodide on silver formanilide explains the behavior of acyl chlorides with the silver salts—a "tautomeric" reaction when compared with our previous knowledge of the action of alkyl halides. It would seem that silver formanilide, for example, reacts giving an acyl derivative, as follows :

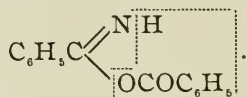
<sup>1</sup> Pinner, in his work "Die Imidoäther," states that an attempt to replace the imide hydrogen in benzimidooisobutylester by heating the ester to  $100^{\circ}$  with ethyl iodide led to no result. He obtained an abundant separation of cyaphenin with a small amount of resin. This result was probably due to the fact that Pinner's ester was not purified by distillation under diminished pressure. When these esters are thus purified some of them do not decompose but can be distilled at ordinary pressure, as shown by Bushong (This JOURNAL, 18, 490) and in previous papers from this laboratory.

<sup>2</sup> Wheeler and Boltwood : This JOURNAL, 18, 381; Wheeler and McFarland: *Ibid.*, 18, 540; Wheeler : *Ibid.*, 18, 695; Wheeler and Walden : *Ibid.*, 19, 129; Wheeler and Metcalf : *Ibid.*, 19, 217; Wheeler, Walden, and Metcalf : *Ibid.*, 20, 64.



The first acyl derivative (A) being unstable, reacts further by addition as above (B), then acetyl chloride separates, the

stable form,  $\text{O}=\text{C}-\text{N}(\text{H})-\text{C}_6\text{H}_5$ , results. The curious fact that silver benzanilide gives with benzoyl chloride benzonitril and benzoic acid, and not dibenzamide, confirms this supposition. The first reaction of the silver salt is a direct replacement of silver by the acyl group. This arrangement being unstable the compound formed decomposes as follows :



It may, however, be stated in general that compounds of the

formula  $\text{ROC}=\text{N} \begin{array}{l} \nearrow \text{R}' \\ \searrow \text{R}'' \end{array}$  are more or less unstable, and readily pass

into the isomeric form  $\text{O}=\text{C} \begin{array}{l} \nearrow \text{R}' \\ \searrow \text{N} \end{array} \text{R}''$ . The ease with which this takes place depends on the character of the groups R, R', and R''. It is therefore not improbable that with suitable groups and the proper regulations of conditions pseudoamides,

$\text{R}'\text{C} \begin{array}{l} \nearrow \text{NR} \\ \searrow \text{OH} \end{array}$ , and imidoacylanhydrides,  $\text{R}'\text{C} \begin{array}{l} \nearrow \text{NR}'' \\ \searrow \text{OCOR}' \end{array}$ , which at present are unknown among acyclic compounds, may be prepared.

#### Experimental Part.

*N*-Ethylformanilide from Silver Formanilide.—25 grams silver formanilide dried over sulphuric acid and which on analysis gave 47.36 per cent. of silver (calculated 47.41 per cent.),

were heated with 22 grams of ethyl iodide<sup>1</sup> to 95°–100° for six hours. An oil resulted which was extracted from the silver iodide by means of dry ether. This gave, on distilling, a product boiling from 257°–267°. (Ethyl phenylimidoformate boils from 213°–215° at ordinary pressure.) This oil was twice distilled. It evidently decomposes to some extent. Two fractions were finally obtained. The first, which was clear and colorless, boiled from 259°–263°; the second from 263°–266° (barometer 772 mm.), the whole material boiling within 7° except a small residue left in the distilling-bulb. The absence of ethyl phenylimidoformate was shown, not only by the boiling-point of the material, but also, by mixing with ortho- and paratoluidine, when no amidines were found. A nitrogen determination in the clear, colorless, inodorous oil (no isonitril odor hence entire absence of formanilide) gave :

	Calculated for $\text{HCONC}_2\text{H}_5 \cdot \text{C}_6\text{H}_5$ .	Found.
N	9.40	9.70

The material is therefore isomeric with the expected ethyl phenylimidoformate. Pictet and Crépieux<sup>2</sup> give the boiling-point of ethylformanilide as 258° at 728 mm. The fact that our material boiled, for the most part, higher than this is due to the difference in barometric pressure.

That our material was ethylformanilide is shown by the fact that on warming with hydrochloric acid and a little alcohol the formyl group separated as ethyl formate, and the resulting solution, on evaporation to dryness, gave a crystalline residue which, when pressed on paper and dried in the air, melted (not sharply) at 173°. Reynolds<sup>3</sup> states that the melting-point of ethylaniline hydrochloride is from 172°–175°. This, on dissolving in ice-water gave, with potassium nitrite, the characteristic nitroso-compound of ethylaniline. There is, therefore, no doubt, that the entire reaction-product was ethylformanilide.

<sup>1</sup> In the experiments in closed tubes we invariably weighed our ethyl iodide in a thin glass tube, which was sealed up as soon as weighed. This, with the imido-ester, was introduced into the larger tube used in heating, and, after this tube had been sealed and cooled, the smaller tube was broken by shaking. In this way we avoided loss by evaporation, and the otherwise unavoidable separation of iodine that always accompanies the sealing of tubes containing ethyl iodide.

<sup>2</sup> Ber. d. chem. Ges., 21, 1108.

<sup>3</sup> Jour. Chem. Soc., 61, 455.



In order to determine whether the silver salt of formanilide reacts more readily with ethyl iodide than the imido-ester under the conditions of the reaction in the closed tube, we heated 15.45 grams of silver formanilide with 9.6 grams of ethyl iodide (about 1 gram less than molecular proportions) to the same temperature and for the same length of time as in the previous experiment. This gave an oil, but not a trace came over at the boiling-point of the imido-ester. It began to boil at about the same temperature as the product of the previous experiment, but the quantity was too small to give a constant boiling-point. The first few drops that came over were mixed with aniline when about sufficient diphenylformamidine for a melting-point determination was obtained. This shows that ethyl phenylimidoformate is more readily acted on in closed tubes than the silver salt.

In another experiment 25 grams of silver formanilide, the same preparation as that used above, and considerable excess of ethyl iodide, were warmed in ether for three days on the water-bath; not all the salt was acted on at this time, but, nevertheless, we obtained about 8 grams of ethyl phenylimidoformate, boiling from  $213^{\circ}$ – $217^{\circ}$ . The higher boiling material was by far the smallest part. This, decomposed with hydrochloric acid and evaporated to dryness, gave a solid mass which was taken up in water, filtered from resin, and then nitrous acid precipitated the nitroso-compound of ethylaniline. It seems, therefore, that ethyl phenylimidoformate suffers rearrangement, to some extent, at ordinary pressure and at the temperature of boiling ether.

*N-Ethylbenzamide from Ethyl Imidobenzoate.*—10 grams of ethyl imidobenzoate and 16 grams of ethyl iodide were sealed up and heated to  $100^{\circ}$  for eight hours, then two or three hours at  $130^{\circ}$ – $160^{\circ}$ . The contents of the tube, after evaporation of the ethyl iodide, distilled almost entirely from  $176^{\circ}$ – $184^{\circ}$  at 20–21 mm. pressure. A few drops distilled below  $176^{\circ}$ . This proved to be benzonitril. The chief product, weighing about 7 grams, was redistilled at ordinary pressure, when it practically all boiled from  $295^{\circ}$ – $296^{\circ}$ . This perfectly colorless oil deposited some crystals. The whole was then taken up in



benzene and filtered from a small amount of material crystallizing in plates and melting from  $123^{\circ}$ – $126^{\circ}$  (benzamide(?)). The benzene solution was evaporated and the oil redistilled. It boiled from  $295^{\circ}$ – $298^{\circ}$  and, on standing over night, deposited a mass of thick, colorless prisms. These, pressed on paper and freed from a little inodorous oil, melted from  $69^{\circ}$ – $70^{\circ}$ .

(The oil is perhaps  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NC}_2\text{H}_5 \\ \searrow \text{OC}_2\text{H}_5 \end{array}$  or  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{N} \begin{array}{l} \nearrow \text{C}_2\text{H}_5 \\ \searrow \text{C}_2\text{H}_5 \end{array} \\ \searrow \text{O} \end{array}$ . It

will be investigated later). The material was crystallized from dilute alcohol when beautiful, long, flattened, colorless prisms developed from the oil which first separated. These melted at about  $69^{\circ}$ . The melting-point of ethylbenzamide is usually given as  $68^{\circ}$ – $69^{\circ}$ . A nitrogen determination gave the result I below.

In another experiment, when an excess of imido-ester was used, the quantity of ethyl iodide being in the proportion of 2 molecules of the ester to 1 molecule of the iodide, the chief product boiled from  $298^{\circ}$ – $299^{\circ}$ . This was analyzed without being allowed to stand. It was free from crystals at first, but on standing solidified. The result on analysis (II below) shows that it is practically identical with the solid I.

	Calculated for $\text{C}_6\text{H}_5\text{CONHC}_2\text{H}_5$ .	I.	Found.	II.
N	9.40	9.11		9.47

The melting-point, appearance, behavior, and analysis therefore agree with those of ethylbenzamide, but Gattermann and Schmidt<sup>1</sup> give the boiling-point of this compound as  $256^{\circ}$ – $260^{\circ}$ . To settle this point we prepared ethylbenzamide by the Schotten-Baumann reaction and found that with 14 grams of material the entire product boiled at 762 mm. pressure from  $298^{\circ}$ – $300^{\circ}$ . This material is identical with the product from ethyl imidobenzoate in all its properties and the boiling-point given by the above authors is far from correct.

A quantitative determination of the products formed in the latter of the above experiments was made as follows: When 15 grams of ethyl imidobenzoate (2 molecules) were heated in

<sup>1</sup> Ann. Chem. (Liebig), **244**, 50.

a closed tube with 7.85 grams of ethyl iodide (1 molecule) for eight hours, a somewhat thick oil or solution resulted which contained minute crystals in suspension. The contents of the tube were diluted with dry ether and the turbid solution filtered. The melting-point of the needles, after they were washed with ether, showed that the material was a mixture or impure. It showed signs of melting at  $120^{\circ}$  and was completely melted at  $203^{\circ}$ . It had the appearance of cyaphenin. The quantity of this material was insignificant, less than 0.2 gram. On evaporating the ether solution an oil was obtained which was distilled at 18–19 mm. pressure. Three portions were then obtained: (1) below  $170^{\circ}$ , 1 gram; (2)  $170^{\circ}$ – $178^{\circ}$ , 9.1 grams; and a residue in smaller quantity above  $178^{\circ}$ , which soon solidified on cooling.

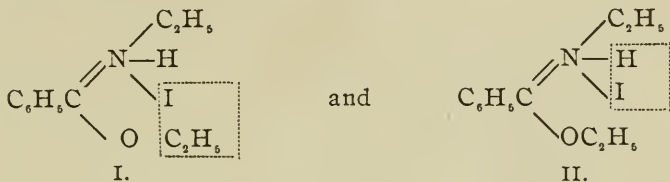
The first fraction proved to be mostly benzonitril; the second or greater portion was redistilled at 762 mm. pressure, when it practically all boiled from  $298^{\circ}$ – $299^{\circ}$ . It was obtained as a strongly refracting colorless oil which, on standing, soon solidified, but not completely, giving beautiful large crystals of ethylbenzamide. The residues from this distillation and that from the distillation under diminished pressure were dissolved in ether and the ether then evaporated. This residue weighed 4.5 grams. It appeared to consist of a mixture of benzamide and ethylbenzamide. It melted at about  $60^{\circ}$ . The material, crystallized from benzene, melted from  $120^{\circ}$ – $126^{\circ}$ . On crystallizing from water it separated in the form of plates and melted at  $128^{\circ}$ . The quantities of the different products, formed in the above experiment, is therefore about as follows:

	Grams.
Benzamide and ethylbenzamide,	4.5
Ethylbenzamide (and diethylbenzamide (?))	9.1
Benzonitril,	1.0
Cyaphenin,	0.2

From this it is apparent that the chief reaction is a rearrangement of the ethyl group from oxygen in the imido-ester to the nitrogen.

The formation of benzamide is to be explained by the decomposition of ethyl imidobenzoate hydriodide, which is

known to decompose into ethyl iodide and benzamide when heated. The formation of this ethyl imidobenzoate hydriodide is due to the separation of hydriodic acid from the addition-product which, as above stated, must be formed as an intermediate product. The reaction of ethyl iodide on ethyl imidobenzoate, therefore, proceeds in two ways, or in other words, the primary addition-product separates chiefly ethyl iodide (Fig. I below), and, to a lesser extent a portion decomposes separating hydrogen iodide (Fig. II), which then unites with the unaltered imido ester :



The ethyl ethylimidobenzoate resulting from the decomposition II is then rearranged with ethyl iodide yielding diethylbenzamide, or remains unaltered, so that one or both of these compounds constitute the oil which accompanies, in small amount, the crystals of ethylbenzamide.

Diethylbenzamide is known to be an oil. The other compound, ethyl ethylimidobenzoate, has not yet been prepared.

We are now engaged in preparing this and similar compounds, in order to determine more positively what the by-products in these reactions are, and we intend to examine the rearrangement of other imido-esters, in general, more thoroughly. We wish to reserve this field for ourselves.

NEW HAVEN, CONN., NOV. I, 1898.

## LXIX.—ON AN ISOMER OF POTASSIUM FERRICYANIDE.

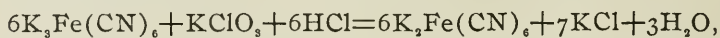
BY JAMES LOCKE AND GASTON H. EDWARDS.

The behavior of potassium ferricyanide toward powerful oxidizing agents has been virtually but once the subject of investigation. In 1869 Städeler,<sup>1</sup> in support of his theory

<sup>1</sup> Ann. Chem. (Liebig), 151, 1.

that the iron in sodium nitroprussiate,  $\text{Na}_2\text{Fe}(\text{CN})_6\text{NO}$ , is tetravalent, sought to obtain the related perferricyanide,  $\text{K}_2\text{Fe}(\text{CN})_6$ , by the action of iodine upon the ferricyanide. He thus obtained a greenish-brown, crystalline product, which was apparently too impure for analysis, for he assigned the above formula to it without having quantitative data upon which to base his conclusions. A body having approximately the same characteristics as Städeler's compound was afterward obtained by Bong,<sup>1</sup> by the action of potassium chlorate and sulphuric acid upon the ferricyanide. To this product was likewise assigned the formula  $\text{K}_2\text{Fe}(\text{CN})_6$ , but it could be prepared only in admixture with a large percentage of potassium sulphate, and no analysis of it was made. The principal work upon the subject, and the only work in which analytical results were obtained, was performed by Skraup in 1877. The latter, to a certain extent, adopted Bong's method, but he substituted hydrochloric acid for sulphuric, and isolated his reaction-product by repeatedly precipitating the aqueous solution with alcohol. He finally obtained a completely amorphous, black or dark-violet powder, which was intensely hygroscopic and smelled strongly of cyanogen. This body Skraup submitted to thorough analysis, but he was unable to obtain satisfactory results. The percentage of cyanogen fell much below the amount calculated for the compound  $\text{K}_2\text{Fe}(\text{CN})_6$  (about 4.0 per cent.). But the iron and potassium, while correspondingly high, were present in the approximate ratio of one to two, and he therefore assumed the body possessed the formula previously suggested by Städeler and Bong.

The details of the method of preparation used by Skraup were briefly as follows: Assuming the reaction to proceed in the simplest manner, *viz.*, according to the equation,



he added to the hot solution of 50 grams potassium ferricyanide and 4 grams of potassium chlorate, in 100 cc. water, the calculated quantity of hydrochloric acid (4 grams, sp. gr. 1.19) in about 75 cc. water. The solution quickly assumed

<sup>1</sup> Bull. Soc. Chim. (1875), 24, 268.

a peculiar red color, and after a few minutes effervescence was observed, presumably escaping cyanogen chloride. Shortly afterwards the solution was cooled down and allowed to stand for twenty-four hours. Precipitation with alcohol then yielded a crystalline product, which was redissolved in water and reprecipitated with alcohol about twelve times. On the third or fourth repetition of this operation the body began to lose its crystalline nature, and the final product, which he used for his analyses, was completely amorphous. The most characteristic reaction of the new compound, and the only one which indicated that its iron was in the tetra-valent state, was found to be its decomposition by alkalis. On being boiled with the latter it yielded ferric hydroxide, potassium ferrocyanide, and potassium cyanate.

The method employed by Skraup is open to criticism at two points. If the reaction proceeds as he supposed, it should be stopped before the evolution of cyanogen chloride begins, for this must be due to the decomposition of the substance. In describing the reactions of the salt, Skraup states that it is slowly decomposed by alcohol. It would hardly seem advisable, therefore, to employ repeated precipitation with alcohol as a means of purifying it. These considerations led us to believe that the final, amorphous body was simply a decomposition-product of the supposedly impure crystalline precipitate obtained on the first addition of alcohol to the oxidized solution, and that this body might perhaps be obtained in a state more suitable for analysis by some other supplementary process.

We therefore prepared this salt according to Skraup's directions, but placed the mixture in ice-water as soon as the first sign of effervescence was observed. The time required for the reaction varies greatly with the temperature. When the hydrochloric acid is added to the boiling solution the gas comes off at once, but at  $95^{\circ}$ , the temperature at which we worked, about five minutes are required. When the solution had cooled to almost  $20^{\circ}$  it was filtered, and slightly less than an equal volume of alcohol, or just enough to bring about incipient precipitation, was added. The solution was



then allowed to stand until its temperature had fallen nearly to  $0^{\circ}$ . A dense crystalline precipitate separated out, from which the mother-liquid was drawn off as completely as possible, without washing, on a suction filter. The product was then redissolved in as little water as possible, and partially reprecipitated with a much smaller volume of alcohol. On a second repetition of this operation, the crystalline nature of the precipitate became less distinct, as Skraup also observed. The purification was therefore carried no further. The salt was extremely soluble in water, yielding a solution which was green by reflected light, and by transmitted light had a peculiar reddish tint. Thus far it corresponded with Skraup's observations, but on boiling with ammonium hydroxide it gave only a trace of ferric hydroxide and potassium ferrocyanide,<sup>1</sup> indicating that our supposition was correct, that Skraup's body was a product of decomposition of his first precipitate.

The salt obtained on the third precipitation with alcohol (the yield was about 1 gram) was carefully examined under the microscope for impurities. It consisted of very small, greenish-yellow needles, among which no foreign ingredients could be seen. The body was, therefore, subjected to analysis, in the expectation that it would give results corresponding closely with the formula  $K_3Fe(CN)_6$ . To our surprise, however, we found that, together with 11.83 per cent. of water, it contained the four elements in the same ratio as potassium ferricyanide itself, corresponding almost exactly with the formula  $K_3Fe(CN)_6$ . The results of this first analysis (I) follow :

	Calculated for $K_3Fe(CN)_6$ with 11.83 per cent. $H_2O$ .	Found.	Ratio.	
$H_2O$	11.83	11.83	....	2.00
Fe	15.01	15.43	0.344	1.03
C	19.30	19.20	1.97	5.91
N	22.51	22.70	2.07	6.21
K	31.35	31.60	1.0	3.0
	100.00	100.76		

<sup>1</sup> A quantitative determination of the ferrocyanide thus formed by titration with potassium permanganate, showed that only 0.07 per cent. of the salt had undergone reduction.



The water present we afterwards found to be due chiefly to the extreme difficulty with which the salt can be dried. On precipitation the latter comes down as a network of very fine, delicate needles, in the capillary spaces between which the water is most obstinately retained. By allowing the salt to stand for several days in a vacuum over sulphuric acid, the percentage of water can be reduced until it corresponds with the value calculated for the formula  $K_3Fe(CN)_6 + H_2O$ .<sup>1</sup> Our first supposition was that the presence of this water was the cause of the difference between the new compound and the normal ferricyanide, or, in other words, that it was water of constitution. This hypothesis, however, is inadmissible; for the corresponding silver salt, which can readily be obtained, is like normal silver ferricyanide—an anhydrous compound, and has the formula  $Ag_3Fe(CN)_6$ . The salt must, therefore, be regarded as an actual isomer of potassium ferricyanide. What the structural difference between the two is, or how the isomer happens to be formed through the action of such a substance as chloric acid, we cannot explain. But repeated analyses of the compound itself, and also of the silver salt, together with the quantitative study of reactions in which it was completely converted into the normal ferricyanide, leave no doubt as to its composition. Its reactions, on the other hand, are in some cases totally different from those of the latter compound. We propose for it, as a temporary designation, the term potassium  $\beta$ -ferricyanide.

The various analyses of the isomer published below were made from as many different preparations obtained under as varied conditions as possible. In the course of the work it was found that two precipitations with alcohol are sufficient to yield the body in a state pure enough for analysis. Even on the first precipitation it is nearly pure, giving no ferric hydroxide when boiled with ammonia and containing only a trace (about 0.5 per cent.) of chlorine. By using somewhat less than an equal volume of alcohol on the second precipitation, a yield of about 15 grams could be obtained, and when the conditions were very carefully observed the individual

<sup>1</sup> Found, 5.55 per cent. The theory requires 5.18 per cent.

crystals were large enough to be observed by the naked eye. A slight variation of the conditions in any particular, however, leads to the formation simply of a crystalline paste, which it is almost impossible to purify. The properly prepared salt can be easily and thoroughly washed with 75 per cent alcohol; when placed in a vacuum, after subsequent washing with absolute alcohol, it falls to an extremely light, voluminous powder. This possesses a pure, rich olive color, which appears brown when observed by gaslight. It dissolves with the utmost ease in water, but unlike Skraup's compound, it is not noticeably hygroscopic. The solution is comparatively stable, though it undergoes gradual decomposition on standing. This decomposition is not accompanied by the formation of either potassium cyanide, hydrocyanic acid or free cyanogen, nor does the dry salt possess the slightest odor of the latter substance.

Various attempts were made to obtain the salt in the form of larger crystals, by the evaporation of its concentrated aqueous solution. But owing to the capillary action of the needles as they separated on the sides of the vessel, only a dense efflorescent growth was obtained, from which no individual crystals could be isolated. Analysis II below is from one of these crops. When a small quantity of the salt is dissolved in a drop or two of water and allowed to crystallize out on an object glass, it is obtained as an intimate network of microscopic needles, of characteristic, very slightly tapering form. They are probably rhombic, showing parallel extinction, and slightly pleachroitic. Among them no trace of the heavy prismatic or block-shaped crystals of the normal or  $\alpha$ -ferricyanide could be detected. In crystallization experiments with mixtures of the two isomers, on the other hand, they could be distinguished at a glance, showing that the new compound is not merely the  $\alpha$ -ferricyanide in a new crystallographic modification.

*Analytical Results.*—For the determination of potassium and iron the compound was decomposed by heating with concentrated nitric acid. The iron was then precipitated with ammonium hydroxide, and the potassium weighed as chloride or

sulphate. The nitrogen was determined by combustion. The total combustion of the carbon takes place with great difficulty, and the results for that element were rather low (one per cent or more). In view of the above determination, (I) however, together with experiments on the quantitative conversion of the compound into potassium  $\alpha$ -ferricyanide, its further determination was deemed unnecessary, and the percentage of cyanogen was calculated from that of the nitrogen. The water was determined by combustion.

II.			III.		
	Found. Per cent.	Ratio.		Found. Per cent.	Ratio.
CN	45.31	6.0		45.13	6.15
Fe	16.95	1.04		16.02	1.01
K	33.91	3.00		32.90	3.00
H <sub>2</sub> O	5.41	1.00		4.65	0.8
	<hr/> 101.47			<hr/> 98.70	

IV.				
	Found.	Ratio.	Average of the 3 analyses.	Calculated for $K_3Fe(CN)_6 \cdot H_2O$ .
CN	45.05	5.94	45.16	44.96
Fe	16.98	1.05	16.65	16.14
K	34.11	3.0	33.64	33.72
H <sub>2</sub> O	4.73	0.87	4.93	5.18
	<hr/> 100.87		<hr/> 100.38	
			<hr/> 100.00	

A subsequent determination of water, according to the method of Jannasch and Locke,<sup>1</sup> in another preparation which had previously been allowed to stand in a vacuum over sulphuric acid for three days, gave 5.55 per cent. There seems to be no doubt, therefore, that the body possesses the formula  $K_3Fe(CN)_6 \cdot H_2O$ . In order to prove this definitely, however, and at the same time make a direct estimation of the cyanogen, a method was sought by which the body could be quantitatively converted to the  $\alpha$ -ferricyanide. Preliminary experiments showed that it passed into potassium ferrocyanide upon reduction, but its titration on that principle, either according to the method of Mohr<sup>2</sup> or after reduction with ferrous

<sup>1</sup> Ztschr. anorg. Chem., 6, 174.

<sup>2</sup> Ann. Chem. (Liebig), 105, 62.

hydroxide, gave no satisfactory results. The most convenient means of reduction we found to be sodium amalgam in alkaline solution. This converted the substance completely into the ferrocyanide, without the separation even of traces of iron. The ferrocyanide was then titrated with potassium permanganate in sulphuric acid solution. The details of the method were first worked out with potassium  $\alpha$ -ferricyanide, and the best conditions found to be as follows: The solution of the salt (about 0.2 gram) in 100 cc. of water, was rendered slightly alkaline with sodium carbonate, and a piece of 5 per cent sodium amalgam was then added. During the reduction the solution was kept on the steam-bath. In the course of an hour or so the mercury was filtered off and the solution cooled and very slightly acidified with sulphuric acid. It was then titrated with a solution of permanganate until the red color of the latter remained for half a minute or more.

With potassium  $\alpha$ -ferricyanide the following results were obtained:

1 cc.  $\text{KMnO}_4$  solution = 0.00572 gram Fe = 0.0336 gram  $\text{K}_3\text{Fe}(\text{CN})_6$ .

	$\text{K}_3\text{Fe}(\text{CN})_6$ taken. Gram.	Cc. $\text{KMnO}_4$ solu- tion used.	Cc. $\text{KMnO}_4$ calculated.
I	0.2596	7.65	7.72
II	0.2402	7.10	7.15
III	0.1926	5.70	5.71

The same method of procedure gave for the new compound the following results:

	$\text{K}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ taken. Gram.	Cc. $\text{KMnO}_4$ solu- tion used.	Cc. $\text{KMnO}_4$ solu- tion calculated.
I	0.1611	4.55	4.55
II	0.2520	7.20	7.11
III	0.1946	5.40	5.49
IV	0.2641	7.35	7.45
V	0.1427	4.10	4.04
VI	0.2208	6.30	6.26

In order to make sure that in these experiments only potassium  $\alpha$ -ferricyanide remained in the solutions, or, in other words, that the conversion of the  $\beta$ -ferricyanide to the latter compound was absolutely quantitative, the amount of

$\alpha$ -ferricyanide which the solutions in V or VI contained was gravimetrically determined. This was accomplished by precipitating the titrated solutions with silver nitrate, and estimating the percentage from the silver, which was weighed as chloride. The results were very exact, the amount of silver found differing by little more than a milligram from that required by theory :

V. Found, 0.1347 gram Ag = 0.1367 gram  $K_3Fe(CN)_6$ .

Calculated, 0.1332 gram Ag = 0.1352 gram  $K_3Fe(CN)_6$ .

VI. Found, 0.2048 gram Ag = 0.2079 gram  $K_3Fe(CN)_6$ .

Calculated, 0.2061 gram Ag = 0.2092 gram  $K_3Fe(CN)_6$ .

The average percentage of cyanogen in the  $\beta$ -ferricyanide, as calculated from these six determinations, is 45.07. The theory requires 44.96 per cent.

Potassium  $\beta$ -ferricyanide, like the normal salt, yields characteristic precipitates with the solutions of most of the heavy metals. These have, in general, the same characteristics as the corresponding  $\alpha$ -ferricyanides, and in some cases *pass over into the latter with extreme ease*. The less notable of these precipitates are collected briefly in the table below, in which, for the sake of comparison, the  $\alpha$ -ferricyanides are also included. The reactions examined were brought about in 2 per cent solutions. In the case of silver, bismuth, stannic tin, and lead, the reactions will be discussed more fully, as they present characteristic points of difference between the two ferricyanic groups.

$\beta$ -Ferricyanides.		$\alpha$ -Ferricyanides.	
Cd.	Dirty green, soluble in $(NH_4)_2CO_3$ , HCl, insoluble in $HNO_3$ .	Pale yellow, soluble in $(NH_4)_2CO_3$ , HCl, insoluble in $HNO_3$ .	
Cu.	Yellowish-green, insoluble in $HNO_3$ or HCl.	Dark greenish-yellow, insoluble in $HNO_3$ or HCl.	
Fe <sup>III</sup> .	Dark yellow coloration, blue precipitate on boiling.	Dark red coloration, blue precipitate on boiling.	
Fe <sup>II</sup> .	Blue precipitate.	Blue precipitate.	
Hg <sup>II</sup> .	No precipitate.	No precipitate.	
Co.	Dark red precipitate, insoluble in HCl or $HNO_3$ .	The same.	



	$\beta$ -Ferricyanides.	$\alpha$ -Ferricyanides.
Mn.	Brown precipitate, insoluble in $\text{NH}_4\text{OH}$ , $\text{HCl}$ , or $\text{HNO}_3$ .	The same.
Hg <sup>1</sup> .	Yellowish-green, flocculent precipitate. Rapidly undergoes reduction on boiling, becoming blue.	Pale yellow, undergoes reduction only slowly on boiling.
Ni.	Dark yellowish-green, insoluble in $\text{HNO}_3$ or $\text{HCl}$ .	Light yellow, same behavior.
Zn.	Yellowish-green, soluble in $\text{HCl}$ , $(\text{NH}_4)_2\text{CO}_3$ , insoluble in $\text{HNO}_3$ .	Yellow, same behavior.

The  $\beta$ -ferricyanides of these metals, as is seen, resemble the  $\alpha$ -compounds in nearly all particulars, being distinguished from them chiefly in having a more or less pronounced green color. It might be supposed, therefore, that they are identical with them, but colored by slight impurities. But the behavior of the salts of bismuth, stannic tin, lead, and silver shows that this is not the case. Bismuth  $\alpha$ -ferricyanide is a very sparingly soluble, straw-colored precipitate, which is deposited even from very dilute solutions of potassium ferricyanide on addition of bismuth nitrate. It is likewise insoluble in concentrated nitric acid. *A solution of potassium  $\beta$ -ferricyanide, on the other hand, when freshly prepared, gives no trace of a precipitate with bismuth nitrate.* The solution assumes a slightly greenish tint, but even when concentrated remains otherwise unaltered for some time. On standing, and especially when exposed to the action of the direct sunlight, it deposits large granules of a black, crystalline compound, which we have not yet fully examined, but which is apparently bismuth ferrocyanide.

Stannic chloride, on the other hand, yields no precipitate with potassium  $\alpha$ -ferricyanide, but precipitates the isomer completely. The resulting compound comes down as a slimy, pure green body, which is insoluble in either hydrochloric or nitric acid. We have, however, been unable to obtain it in a state suitable for analysis.

A comparative study of the lead salts was kindly under-



taken by Mr. H. A. North. While lead ferricyanide is not precipitated by potassium  $\alpha$ -ferricyanide, under ordinary circumstances, it is much less soluble in water than either the latter compound or lead nitrate. When concentrated solutions of the two are mixed in the proper proportions it slowly separates out in large, dark-red crystals.<sup>1</sup> Mr. North made this salt by dissolving the calculated quantities, or 3 grams each, of potassium ferricyanide and lead nitrate in 7 cc. and 8 cc. of water, respectively. On allowing the mixed solutions to stand for a few minutes, he obtained more than a gram of well-crystallized lead ferricyanide. A similar experiment was then made, with exactly the same quantities, potassium  $\beta$ -ferricyanide being used instead of the  $\alpha$ -salt. No crystallization took place, indicating that lead  $\beta$ -ferricyanide is much more soluble in water than its isomer. This solution was allowed to stand over night, and by morning, in addition to an efflorescent product, more or less of the normal lead  $\alpha$ -ferricyanide had crystallized out, the  $\beta$ -ferricyanide having partially passed over into the latter compound. The solution then gave the usual straw-colored precipitate with bismuth nitrate, with which it had not reacted twelve hours before.

Various attempts were made to isolate the  $\beta$ -lead salt by other means, but without much success. The most satisfactory results were obtained by dissolving lead oxide in glacial acetic acid, and adding to the solution the calculated quantity of potassium  $\beta$ -ferricyanide, dissolved in 25 cc. of glacial acetic acid and 7 cc. of water. A green, amorphous precipitate separated out, which was readily soluble in water forming a greenish-red solution, and this yielded no precipitate with bismuth nitrate. An analysis of the product showed that it contained 49 per cent lead, and no potassium, but no simple atomic ratio was evident between the lead and nitrogen, which was somewhat low. It is probable, therefore, that the body was a mixture. An experiment made with potassium  $\alpha$ -ferricyanide, in a similar manner, yielded a crystalline precipitate of the ordinary lead ferricyanide.

The most interesting  $\beta$ -ferricyanide of a heavy metal which

<sup>1</sup> Rammelsberg : J. prakt. Chem. (2), 39, 455.



neither filtrate could either hydrocyanic or cyanic acid be detected. The change which the silver salt undergoes on heating must therefore be assumed to take place without the formation of any substance other than silver  $\alpha$ -ferricyanide, and to consist simply in a rearrangement of atoms in the molecule  $\text{Ag}_3\text{Fe}(\text{CN})_6$ .

It was hoped that by acting on the silver salt with the calculated quantity of hydrochloric acid the free  $\beta$ -ferricyanic acid could be prepared. The solution obtained gave for the moment no precipitate with bismuth nitrate, showing that the  $\beta$ -acid had been formed, but the latter passed within a few minutes into the normal acid, and then into further decomposition-products. Efforts to prepare the salts of calcium and barium in the same way also failed, the normal ferricyanides being finally obtained.

In regard to the constitution of the  $\beta$ -ferricyanic group we have little to state. Any attempt to assign a definite structural formula to it would, for the present, be pure speculation. The suggestion offers itself that one of the two isomers contains isonitril groups, the other nitril groups. But this view, at least, is absolutely refuted by the identical behavior of the two on reduction. So far as we can find, there are no cases known where isomers containing respectively the  $-\text{CN}$  and  $-\text{NC}$  groups yield the same product with nascent hydrogen. On the other hand, if both ferricyanides contain only cyano-gen groups, the  $\beta$ -compound becomes of especial importance because of its bearing on Werner's theory. According to the latter the ferricyanic group is not to be represented by the structural formula, but simply as a radical in which the cyano-gen groups occupy "coordination positions" about the ferric atom. Isomerism between two equivalent  $\text{Fe}(\text{CN})_6$  groups, if this is so, can be due only to stereochemical causes. The greatest value of Werner's theory lies in the explanation which it offers of the cases of isomerism among the platinum-amine and cobalt-amine compounds. The six coordinated groups are supposed to occupy the angles of a regular octahedron, in the center of which is the metal. Isomerism is then possible whenever two or more of the coordinated groups

differ from the others. But according to it a radical in which they are all alike, such as  $\text{Fe}^{\text{III}}(\text{CN})_6$ , cannot have two different configurations, or in other words, exist in isomeric modifications. It would seem, therefore, that the existence of potassium  $\beta$ -ferricyanide stands in direct contradiction to such a theory, at least in its present form.

It may of course be that the  $\beta$ -ferricyanide is a mixture of two substances in proportions giving the atomic ratio  $\text{K}_3\text{Fe}(\text{CN})_6$ . But throughout all our investigations we have searched for, and failed to find, a single indication that such is the fact. Its completely crystalline and homogeneous appearance, the constant composition of different products, and all its observed reactions point closely to its being an individual chemical compound. Our investigations will be continued, however, and we hope to bring more light to bear upon the subject within a short time.

NEW HAVEN, December 12, 1898.

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## REACTION OF ORTHODIAZOBENZOIC ACID WITH SULPHUROUS ACID AND COPPER POWDER.

BY W. E. HENDERSON.

The work described in the following article was undertaken in the chemical laboratory of the Johns Hopkins University for the purpose of testing the truth of the statement not infrequently found in the literature, particularly in text-books and chemical dictionaries, that sulphonic acids result from the decomposition of diazo compounds in the presence of sulphurous acid, especially if copper powder or cuprous hydroxide is present in the solution.<sup>1</sup>

If such a reaction is a general one, it was thought to be desirable to ascertain the conditions most favorable for successfully employing it, as it would possess considerable interest from a theoretical as well as from a practical standpoint. For although there have been a number of methods devised for

<sup>1</sup> Watts' Dictionary: "Sulphonic Acids"; Meyer and Jacobson's *Lehrbuch*, II, 294; Bernthsen's *Org. Chem.* (McGowan's Trans.), p. 397; Hübner: *Ber. d. chem. Ges.*, 10, 1715; Müller and Wiesinger: *Ibid.*, 12, 1348; Landsberg: *Ibid.*, 23, 1454.

introducing into an aromatic nucleus group containing sulphur, which can be converted into sulphonie acid residues, few of these methods are very satisfactory, and we are forced to depend, for the most part, on methods of direct sulphonation for obtaining sulphonie acids. This often leaves in doubt the question as to which position the entering group occupies, and a practical method for replacing any group of known position by a sulphonie acid group, would be of much interest in deciding cases of doubtful orientation by synthesis.

Many attempts have been made to replace an amido group, with some group containing sulphur by employing a diazo decomposition. The results have been quite varied and in general unsatisfactory; for although many definite products have been obtained, the main reaction has been complicated by many secondary ones, due to the reducing power of the sulphur compounds employed. Chief among these substances have been hydrogen sulphide,<sup>1</sup> alkali sulphides,<sup>2</sup> sulphurous acid,<sup>3</sup> mercaptans and sulphides,<sup>4</sup> and thiocarbonic ethers.<sup>5</sup> The products have been sulphides, hydrosulphides, or sulphonie acids in very small quantity, and the methods have not promised much in a practical way.

Gattermann,<sup>6</sup> in his paper on diazo decompositions in the presence of various free acids and copper powder, suggested that by employing sulphurous acid, sulphonie acids would probably result, but he did not subsequently follow up this suggestion.<sup>7</sup>

Preliminary experiments showed that, under ordinary circumstances at least, sulphonie acids do not result from this reaction, but other substances, difficult to isolate owing to their solubility, are formed. Hence orthoaminobenzoic acid was selected as the material for study, in the hope that the

<sup>1</sup> Tassinari : *Gaz. chim. Ital.*, **22**, 504; Griess : *Ann. Chem. (Liebig)*, **137**, 74.

<sup>2</sup> Graebe and Mann : *Ber. d. chem. Ges.*, **15**, 1688; Griess : *Ann. Chem. (Liebig)*, **137**, 74; Klason : *Ber. d. chem. Ges.*, **20**, 349; Purgotti : *Gaz. chim. Ital.*, **20**, 30.

<sup>3</sup> Hübner : *Ber. d. chem. Ges.*, **10**, 1715; Müller and Wiesinger : *Ibid.*, **12**, 1348; Landsberg : *Ibid.*, **23**, 1454.

<sup>4</sup> Stadler : *Ibid.*, **17**, 2078.

<sup>5</sup> Leuckart : *J. prakt. Chem. [II]*, **41**, 179.

<sup>6</sup> Gattermann : *Ber. d. chem. Ges.*, **23**, 1218.

<sup>7</sup> After the results described in this paper had been obtained, the paragraph in *Centralblatt*, 1898, II, 196, came to my attention.



carboxyl group would render the product of the reaction easy to obtain and identify. This proved to be the case, and the product obtained was found to be dithiosalicylic acid,  $[\text{C}_6\text{H}_4\cdot\text{COOH}]_2\text{S}_2$ .

On adding a solution of orthodiazobenzoic acid sulphate to a cold, saturated solution of sulphurous acid in which copper powder was suspended, nitrogen was at once evolved. The reaction was a very clean one, free from all the tarry products, which so often accompany reactions of this kind. Quite an amount of copper passed into solution as the reaction proceeded, forming a mixture of cuprous and cupric salts, and a part of the sulphurous acid was oxidized to sulphuric. The reaction is therefore accompanied by an extensive reduction, and instead of obtaining orthosulphobenzoic acid, dithiosalicylic acid is the chief product. It is probable that both the corresponding sulphinic acid and thiosalicylic acid could be obtained by suitable methods, but no effort was made to isolate them. The yield of dithiosalicylic acid was about 50 per cent. of the theoretical.

Inasmuch as the dithio-acid yields orthosulphobenzoic acid on oxidation with potassium permanganate, the main purpose in view was not entirely defeated by this unexpected result. I shall study the reaction further, both in the case of other amido compounds, which preliminary experiments show to act generally in the same way, and as to the yield of sulphonic acids that can be obtained by oxidation of the raw product.

#### EXPERIMENTAL PART.

Five grams orthoaminobenzoic acid were dissolved by warming in a solution of 6 grams sulphuric acid (sp. gr. 1.84) in 40 cc. water, and the solution was cooled to  $5^\circ$ . During the cooling the solution was constantly stirred so that the crystals of anthranilic acid sulphate which separated, might be as small as possible. To this solution was added slowly from a dropping-funnel, a solution of 3 grams sodium nitrite, until, after stirring for some time, the solution colored starch iodide paper, and all the crystals of anthranilic acid sulphate were dissolved.



The solution of orthodiazobenzoic acid sulphate so prepared was then added, from a dropping-funnel, to a cold, saturated solution of sulphurous acid (about 200 cc.) in which 30 grams of copper powder had been suspended. The solution was contained in a good-sized flask to facilitate constant shaking so that the copper might not settle to the bottom. Nitrogen was at once evolved, and the solution assumed an emerald-green color. On standing for some time or by heating on the water-bath, a voluminous, colorless precipitate was slowly thrown down, which proved to be dithiosalicylic acid. The precipitation was slow, and apparently incomplete, so that it was found best to obtain the acid in the following way :

After filtering off the excess of copper powder, barium carbonate was added to the hot solution as long as it produced a dark-colored precipitate, which first appears when most of the free acid has been neutralized. This appears to be, for the most part, the copper salt of dithiosalicylic acid, together with other copper compounds. The insoluble substances were filtered off and warmed with hydrochloric acid. This dissolved the excess of barium carbonate, the barium sulphite, and the copper compounds, and left the barium sulphate and the insoluble dithiosalicylic acid on the filter. On digesting the mixture with sodium hydroxide, the latter acid was dissolved with formation of its sodium salt, and the free acid was regained, as an amorphous precipitate, by pouring the filtrate from the barium sulphate into an excess of hydrochloric acid.

The chief reactions of this acid, together with the properties of its principal salts, its chloride, and its methyl and ethyl ethers have recently been described by List and Stein,<sup>1</sup> who obtained it by the reduction of the unsymmetrical chloride of orthosulphobenzoic acid, an account of whose work came to hand during the progress of this study. These details need not, therefore, be repeated here. The acid was fully identified by its agreement with their description and by an analysis.

I. 0.1880 gram substance gave 0.3770 gram  $\text{CO}_2$ , and 0.0567 gram  $\text{H}_2\text{O}$ .

II. 0.2428 gram substance gave 0.3720 gram  $\text{BaSO}_4$ .

<sup>1</sup> List and Stein: Ber. d. chem. Ges., 31, 1666.

	Calculated for (C <sub>6</sub> H <sub>4</sub> COOH) <sub>2</sub> S <sub>2</sub> .	Found.
C	54.90	54.63
H	3.26	3.35
S	20.91	21.06

The chloride crystallized from benzene in thick, yellow needles or prisms and melted at 154°. The methyl ester, made by boiling the chloride in methyl alcohol, melted at 131°.

My thanks are due to Dr. Stieglitz, of the Kent Laboratory at Chicago, for many courtesies shown me while working in his laboratory.

ATHENS, OHIO, December, 1898.

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Contributions from the Chemical Laboratory of Purdue University.

## DIRECT NITRATION OF THE PARAFFINS.

BY R. A. WORSTALL.

In a previous communication<sup>1</sup> were given the results of a preliminary investigation of the action of nitric acid upon the paraffins, showing that the action of nitric acid without pressure results in the formation of primary mono- and dinitro-paraffins, together with oxidation-products which, for the hydrocarbons studied, were found to be the same in all cases; namely, carbonic, acetic, succinic, and oxalic acids.

A more careful investigation of these reactions, repeating the experiments with the three hydrocarbons previously studied, and extended so as to include other paraffins, has been made, in order to ascertain the limits of the reaction, and the quantitative yield of nitro-products obtainable from each hydrocarbon, while more attention has been paid to the oxidation-products. This investigation has confirmed, in all essential particulars, the statements made in the preliminary paper.

The source of all the hydrocarbons studied has been American petroleum, all save one of them, either in the crude or refined state, having been secured through the kindness of Dr. C. F. Mabery. The method of purification has been the same

<sup>1</sup> This JOURNAL, 20, 202.

for each—namely, agitation with fuming sulphuric acid, washing with caustic soda, drying, and fractioning over metallic sodium, in many cases as often as thirty times, until a good separation was obtained.

Unless otherwise stated, the method of nitration has been in each case as follows: The hydrocarbon was boiled with nitric acid of proper concentration in a flask fitted with return-condenser, until the acid was exhausted. The spent acid was then drawn off and fresh acid added, the operation being repeated until a considerable quantity of the hydrocarbon appeared to have been converted into nitro-products. The oil was then drawn off, washed, dried, and the unchanged hydrocarbon distilled off, leaving the high-boiling nitro-compounds as a residue. The process was repeated with the unchanged hydrocarbon as long as necessary. The mixed nitro-paraffins were separated by distilling in steam, in which only the mononitroparaffins are volatile. Oxidation-products were sought for in the escaping gases and in the spent acid.

*Hexane, C<sub>6</sub>H<sub>14</sub>.*

Normal hexane (boiling-point 68°–69°, specific gravity 0.6860 at  $\frac{20}{20}^{\circ}$ ) reacts with fuming nitric acid and with mixed sulphuric and fuming nitric acids, but there is no apparent reaction when nitric acid of specific gravity lower than 1.45 is employed. Even with nitric acid of specific gravity 1.60 the reaction is very slow, but in time the hydrocarbon is completely transformed into nitro- and oxidation-products.

Two hundred and fifty grams hexane were treated with five successive portions of 200 grams each of fuming nitric acid, sp. gr. 1.60, being boiled with each portion eight hours. The loss through oxidation amounted to 70 grams, and the yield of mixed nitro-products to 13 grams. By continuing the nitration the average yield has been 10 per cent of the theoretical of mixed nitro-products, about 6 per cent nitrohexane, and 4 per cent dinitrohexane. Through a misprint (unfortunately overlooked until too late) the statement made in the preliminary paper in regard to the yield of nitrohexane was entirely wrong. No such yield as there stated (60 per cent) has been at any time obtained.

*Oxidation-products.*

Numerous tests have failed to show the presence of more than four oxidation-products—acetic, succinic, carbonic, and oxalic acids. In boiling these hydrocarbons with nitric acid there is a persistent odor of butyric acid noticeable in the spent acid, especially in the case of the higher-boiling paraffins. The dinitroparaffins have a butyric-like odor, and from inability to detect the presence of any fatty acid higher than acetic, it was concluded that the odor was due to these dinitroparaffins.

*Acetic Acid.*—A portion of the spent acid was neutralized with sodium carbonate, acidified slightly with sulphuric acid, and distilled in steam. Free nitrous acid in the distillate was destroyed by a dilute solution of potassium permanganate, and the distillate then neutralized with calcium carbonate, and filtered. Silver acetate was precipitated in the filtrate by means of silver nitrate, and the precipitate dissolved in hot water and crystallized. A silver determination showed the salt to be pure silver acetate.

0.0991 gram gave, on ignition, 0.0635 gram Ag.

	Calculated for $\text{CH}_3\text{COOAg}$ .	Found.
Ag	64.67	64.09

*Oxalic Acid.*—Upon concentrating the spent acids on the steam-bath, and cooling, oxalic and succinic acids separated as crystals. The mixed acids were recrystallized several times from hot water, fine crystals of each being obtained pure. A portion of the oxalic acid was converted into the calcium salt and the latter analyzed.

0.3151 gram gave 0.1360 gram  $\text{CaO}$ .

	Calculated for $\text{CaC}_2\text{O}_4$ .	Found.
Ca	31.25	30.83

*Succinic Acid.*—The succinic acid was easily identified by its melting-point ( $176^\circ$ ) and by many qualitative tests. Its ammonium salt gave a white precipitate with alcoholic barium chloride, and a red-brown precipitate with ferric chloride in the cold.

*Carbonic Acid.*—Carbonic acid was detected in the gases es-

caping from the nitration-flask, by the formation of precipitates with solutions of barium and of calcium hydroxides.

The total yield of oxidation-products other than carbonic acid did not exceed 5 per cent. The latter, however, must have formed by far the chief product of the reaction.

*Heptane, C<sub>7</sub>H<sub>16</sub>.*

The heptane employed was the normal hydrocarbon (boiling-point 98°–99°, specific gravity 0.6980 at  $\frac{20}{20}^{\circ}$ ).

Nitric acid of specific gravity 1.42, mixed sulphuric and nitric acids, and fuming nitric acid all react with heptane to form nitro-derivatives. The nitric acid of specific gravity 1.42 gives the best yield of mononitroheptane, the action of the mixed acids resulting in the formation of considerable dinitroheptane, that of the fuming nitric acid in greater oxidation.

The method of nitration and of separating the products was the same as before described. Three hundred and fifty grams heptane treated for ninety-four hours with 1200 grams nitric acid (1.42 sp. gr.) gave 80 grams nitroheptane, 16 per cent of the possible theoretical yield, and 90 grams of dinitroheptane, 24 per cent of the possible theoretical yield, the total yield of nitro-products, therefore, amounting to 40 per cent of the theoretical.

The oxidation-products were the same as in the case of hexane.

*Acetic Acid.*—The acetic acid was separated from a portion of the waste acids in the manner previously described. The silver salt was analyzed.

0.0473 gram gave, on ignition, 0.0305 gram Ag.

	Calculated for CH <sub>3</sub> COOAg.	Found.
Ag	64.67	64.50

*Oxalic Acid.*—Oxalic and succinic acids were separated from the waste acids and from each other in the manner previously described. The calcium oxalate was analyzed.

0.0480 gram gave, on ignition (with sulphuric acid), 0.0511 gram CaSO<sub>4</sub>.

	Calculated for $\text{CaC}_2\text{O}_4$ .	Found.
Ca	31.25	31.45

*Succinic Acid.*—The succinic acid was recognized by its melting-point and the qualitative tests mentioned under hexane.

*Carbonic Acid.*—Carbonic acid was detected by the usual test in the gases escaping from the nitration-flask. It must have constituted fully 70 per cent of the total products, the other oxidation-products not appearing to exceed 5 per cent.

*Octane,  $\text{C}_8\text{H}_{18}$ .*

Normal octane (boiling-point  $123^\circ$ – $125^\circ$ , specific gravity 0.7123 at  $\frac{20}{20}^\circ$ ) reacts with nitric acid of specific gravity as low as 1.070 with the formation of nitro-products. Nitric acid of specific gravity 1.14 gave the best results, as a larger yield of nitrooctane can be obtained by acid of this concentration, and with less oxidation than by using more concentrated acid. Two hundred and eighty grams octane treated for forty-two hours with 1100 grams of this acid gave 70 grams nitrooctane, 17.5 per cent of the possible theoretical yield, and 125 grams dinitrooctane, 25 per cent of the possible theoretical yield, a total of 42.5 per cent of the theoretical.

The usual oxidation-products resulted.

*Acetic Acid.*—The acetic acid was separated as described under hexane, and the silver salt analyzed.

0.0457 gram gave, on ignition, 0.0296 gram Ag.

	Calculated for $\text{CH}_3\text{COOAg}$ .	Found.
Ag	64.67	64.75

*Oxalic Acid.*—Oxalic and succinic acids were obtained from the spent acid in the manner previously described. The calcium oxalate was analyzed.

0.2743 gram gave 0.1190 gram  $\text{CaO}$ .

	Calculated for $\text{CaC}_2\text{O}_4$ .	Found.
Ca	31.25	30.98

In all, 10 grams of oxalic acid were obtained from the 280 grams octane.



*Succinic Acid.*—The succinic acid was readily recognized by its melting-point ( $175^{\circ}$ ) and by its qualitative reactions. About 3 grams of succinic acid were obtained.

*Carbonic Acid.*—The carbonic acid was detected in the usual way, and must have been equivalent to nearly 60 per cent of the total product, the other oxidation-products not exceeding 5 per cent.

*Nonane, C<sub>9</sub>H<sub>20</sub>.*

The nonane employed was the normal hydrocarbon (boiling-point  $150^{\circ}$ – $151^{\circ}$ , specific gravity 0.7277 at  $\frac{20}{20}^{\circ}$ ). Even very dilute nitric acid acts upon nonane with the formation of nitro-derivatives. For the preparation of nitrononane, nitric acid of specific gravity 1.080 was employed, the method of nitration and of separating the products being the same as previously described. Two hundred and sixty-eight grams nonane treated for forty-two hours with 1200 grams of nitric acid of specific gravity 1.080 gave 80 grams nitrononane, 22 per cent of the possible theoretical yield, and 210 grams dinitrononane, 48 per cent of the possible theoretical yield, a total yield of nitro-products amounting to 70 per cent of the theoretical.

As usual, the oxidation-products were acetic, carbonic, succinic, and oxalic acids.

*Acetic Acid.*—The acetic acid was separated in the usual way and the silver salt analyzed.

0.0652 gram gave, on ignition, 0.0418 gram Ag.

	Calculated for CH <sub>3</sub> COOAg.	Found.
Ag	64.67	64.11

*Oxalic Acid.*—The calcium salt of the oxalic acid was analyzed.

0.3334 gram gave 0.1450 gram CaO.

	Calculated for CaC <sub>2</sub> O <sub>4</sub> .	Found.
Ca	31.25	31.07

About 4 grams of oxalic acid were obtained from the 268 grams nonane.

*Succinic Acid.*—Much more succinic acid was formed from

nonane than from any other hydrocarbon. Each time, upon cooling the spent acid in the nitration-flask, considerable succinic acid crystallized out, in all about 7 grams being obtained.

*Carbonic Acid.*—Carbonic acid was detected as usual in the escaping gases, and probably did not exceed 30 per cent. of the total products.

*Decane, C<sub>10</sub>H<sub>22</sub>.*

The decane employed was the normal hydrocarbon,<sup>1</sup> (boiling-point 175°, specific gravity 0.7398 at 20°). Fuming nitric acid and mixed sulphuric and nitric acids, are without action upon decane in the cold. When heated, however, quite dilute nitric acid will nitrate the hydrocarbon, acid of specific gravity 1.080 giving the best results. The instability of nitrodecane at the temperature of boiling decane prevented the employment of the method previously followed for the separation of the nitro-products. The layer of oil was separated from the spent acid, washed well, then dried, and thin strips of metallic sodium added. By this means all nitroparaffins were slowly converted into sodium salts. The latter were washed out with water, and the residual paraffin again nitrated. For the separation of the nitroparaffins from their salts, the method of Konowalow<sup>2</sup> was employed. The aqueous solution of the sodium salts was saturated with carbon dioxide, the liberated nitroparaffins extracted with ether, and the ether distilled off. By distilling this mixture of mono- and dinitrodecane in steam, the former was obtained pure, but the dinitrodecane decomposed. Twenty grams decane, treated for twelve hours with nitric acid of specific gravity 1.080, without attempting to convert all the hydrocarbon into nitro-products, gave 10 grams nitrodecane, about 35 per cent of the theoretical yield. With larger quantities of the hydrocarbon, carrying the reaction to completion, better yields could no doubt be obtained.

*Hendecane, C<sub>11</sub>H<sub>24</sub>.*

Hendecane (boiling-point 196°, <sup>3</sup> specific gravity 0.7521 at

<sup>1</sup> Mabery : This JOURNAL, 19, 448.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Mabery : *Loc. cit.*

20°) is not acted upon by fuming nitric acid in the cold. When gently boiled with nitric acid of specific gravity 1.080, nitration readily results. Twenty grams hendecane were heated for six hours with 100 grams of 1.080 nitric acid, and the nitroparaffins separated as described under decane. While not all the hydrocarbon had been nitrated by this treatment, nearly 8 grams of nitrohendecane were obtained, and the dinitroparaffin was decomposed.

*Dodecane, C<sub>12</sub>H<sub>26</sub>.*

Dodecane (boiling-point 216°)<sup>1</sup> is slowly acted upon by fuming nitric acid in the cold, with the formation of nitro-products. Twenty-five grams of the hydrocarbon were heated with 100 grams of nitric acid (specific gravity 1.080) for six hours. The nitroparaffins were separated as in the case of the two preceding hydrocarbons. The nitrododecane as obtained by distilling in steam was impure, containing some free hydrocarbon, and the quantity obtained was too small to permit purification. In the case of the last three hydrocarbons, no attention was paid to oxidation-products because of the doubtful purity of these higher distillates of petroleum.

Francis and Young,<sup>2</sup> in giving the results of their study of the action of fuming nitric acid upon petroleum distillates, state that normal nitroparaffins could not have been formed to any appreciable extent, for on diluting the spent acid no nitro-compounds were precipitated. As a matter of fact, the nitroparaffins thus formed are not to be found in the spent acid. In the course of this work it has frequently been noted that when even from 50 to 75 per cent of the hydrocarbon had been converted into nitroparaffins, the latter still floated as an oily layer above the acid, and upon diluting the latter no more than traces of nitro-compounds were precipitated, the latter invariably being dinitroparaffins.

Acetic, succinic, oxalic, and carbonic acids would seem to be the normal products resulting from the oxidation of any paraffin by nitric acid. Even after 75 per cent of the original hydrocarbon had been converted into nitro- and oxida-

<sup>1</sup> Mabery : *Loc. cit.*

<sup>2</sup> Jour. Chem. Soc., 1898, 928.

tion-products, the residual paraffin, when boiled with nitric acid, still gave the same oxidation-products. This fact would seem to show that the latter are not due to the oxidation of naphthenes or other foreign hydrocarbons.

LAFAYETTE, IND., Dec., 1898.

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## HIGHER PRIMARY NITROPARAFFINS.

BY R. A. WORSTALL.

To Victor Meyer and his pupils we are indebted for most of our knowledge of the nitroparaffins from nitromethane to nitropentane, inclusive. These lower nitroparaffins are readily obtained by Victor Meyer's method, the action of silver nitrite on the alkyl iodides, and their properties and derivatives have been well worked out.

Of the primary nitroparaffins above nitropentane, however, but few have ever been made, and even of these little is known. Two causes have operated to make the preparation of the higher nitroparaffins exceedingly difficult. The first is the extreme difficulty attendant upon the preparation of the alkyl iodides necessary for the reaction, and the second is the fact that even after this necessary material has been prepared, the yield of nitroparaffins is small, in consequence of the simultaneous formation of the isomeric nitrous ethers, while it seems almost impossible to free the nitroparaffins from these ethers. Nor are the items of time and expense inconsiderable obstacles to their preparation.

Chancel,<sup>1</sup> by the action of nitric acid on methylhexylketone, obtained dinitrohexane. Beilstein and Kurbatow,<sup>2</sup> by the action of nitric acid on a fraction of American petroleum boiling at 95°–100°, obtained what was doubtless nitroheptane. They attributed its formation to naphthenes. Eichler<sup>3</sup> prepared nitrooctane from octyl iodide and silver nitrite and studied its properties and a few of its derivatives. These seem to be the only recorded instances of the preparation of primary nitroparaffins above nitropentane.

<sup>1</sup> Compt. rend., **94**, 399.

<sup>2</sup> Ber. d. chem. Ges., **13**, 2029.

<sup>3</sup> *Ibid.*, **12**, 1883.

Konowalow<sup>1</sup> has shown that when the paraffins are heated in sealed tubes with dilute nitric acid, secondary and tertiary nitroparaffins result. The preceding paper describes a method for the preparation of primary mono- and dinitroparaffins above and including nitrohexane, and by this method the nitroparaffins herein described were made. The reaction and derivatives described in this paper have been chiefly those which would help to establish the structure of the nitroparaffins. Other derivatives have been prepared and at least one new reaction noted, and these are retained for later papers.

*Nitrohexane*,  $C_6H_{13}NO_2$ .

The nitrohexane separated from the dinitrohexane by distillation in steam (page 211) was dried and fractioned. The greater portion distilled at  $180^\circ$ – $181^\circ$ , and analysis showed it to be pure.

0.2062 gram gave 22.0 cc. nitrogen at 741 mm. and  $23^\circ$ .

0.1154 gram gave 0.2316 gram  $CO_2$ , and 0.1010 gram  $H_2O$ .

	Calculated for $C_6H_{13}NO_2$ .	Found.
C	54.96	54.73
H	9.92	9.74
N	10.72	10.93

*Properties.*—Nitrohexane is a nearly colorless liquid of pleasant, ester-like odor. Its boiling-point is  $180^\circ$ – $181^\circ$  (uncorr.); its specific gravity 0.9605 at  $17^\circ$ . It is insoluble in water, readily soluble in alcohol, ether, and other organic solvents. Like nitropentane<sup>2</sup> it is only very slowly soluble in concentrated aqueous solutions of caustic soda or caustic potash, thus differing from the lower nitroparaffins. It is readily soluble in alcoholic sodium or potassium hydroxide. It is not explosive. With potassium nitrite, sulphuric acid, and potassium hydroxide it gives the nitrolic acid reaction characteristic of primary nitroparaffins.

*Sodium Nitrohexane*,  $C_6H_{13}NO_2Na$ .—For the preparation of sodium salts of the lower nitroparaffins, V. Meyer<sup>3</sup> found two methods which gave pure products. The one was to dissolve

<sup>1</sup> Compt. rend., 114, 26.

<sup>2</sup> V. Meyer: Ann. Chem. (Liebig), 171, 44.

<sup>3</sup> Loc. cit., p. 29.



the nitroparaffin in alcohol and add alcoholic sodium hydroxide. The sodium salt being insoluble in alcohol is precipitated, and can readily be purified. The other method was to dissolve the nitroparaffin in benzene and add strips of metallic sodium. The salt thus formed was pure. The former method is not applicable to these higher nitroparaffins for the reason that all their alkaline salts are readily soluble in alcohol. And the second method is unsatisfactory. For while the action of the metallic sodium on the nitroparaffin in solution in benzene or petroleum ether gives the sodium salt, the latter is usually impure. The metallic sodium seems partially to decompose the nitroparaffin even in the cold, ammonia and sodium nitrite being among the products.

A method was found, however, which gave satisfactory results. The nitroparaffin is dissolved in petroleum ether, and to this solution is added a solution of sodium ethylate made by largely diluting an alcoholic solution of sodium ethylate with petroleum ether. The precipitated sodium salt, when filtered off and washed several times with boiling petroleum ether containing some alcohol, is usually pure.

Analysis of the sodium nitrohexane gave the following result :

0.1345 gram gave 0.0620 gram  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{C}_6\text{H}_{12}\text{NO}_2\text{Na}$ .	Found.
Na	15.03	14.93

*Properties.*—Sodium nitrohexane is a white salt, readily soluble in water and in alcohol, insoluble in ether, carbon disulphide, etc. It usually separates from solvents as a gelatinous mass, but can with difficulty be crystallized from alcohol in fine, silky needles. It blackens when heated but is not explosive.

With solutions of certain metallic salts, sodium nitrohexane gives characteristic results. The silver precipitate is yellow, rapidly turning black. Cupric sulphate gives a green precipitate. Mercuric chloride a yellow precipitate. With solution of ferric chloride an intense red coloration results. Konowalow<sup>1</sup> has shown this to be a characteristic reaction for all primary and secondary nitroparaffins.

<sup>1</sup> Ber. d. chem. Ges., 28, 1851.



Strong acids do not liberate the nitroparaffin from its sodium salt. While the reaction was not investigated it is doubtless analogous to that shown by Nef<sup>1</sup> to take place with sodium nitroethane.

*Hexylamine*,  $C_6H_{13}NH_2$ .—When nitrohexane is gently warmed with iron filings and dilute acetic acid, hexylamine is formed. More vigorous methods of reduction, such as boiling with iron and acetic acid, or with tin and hydrochloric acid, result in total or partial decomposition with the formation of ammonia. The same fact was noted by V. Meyer<sup>2</sup> in the reduction of nitroethane. The hexylamine liberated from the solution by adding caustic soda and distilling in steam was a strong base, giving the isonitril reaction for a primary amine. Its chlorplatinate is sparingly soluble in water. Analysis of the latter salt gave the following result :

0.0110 gram gave, by ignition, 0.0034 gram Pt.

	Calculated for $(C_6H_{13}NH_2Cl)_2PtCl_4$ .	Found.
Pt	30.47	30.90

*Action of Hydrochloric Acid*.—As a primary nitroparaffin, nitrohexane, when heated with concentrated hydrochloric acid to about  $125^\circ$ , should yield hexoic acid and hydroxylamine, while secondary or tertiary nitroparaffins would yield resinous products.<sup>3</sup>

About 5 grams nitrohexane were heated in a sealed tube with 10 grams concentrated hydrochloric acid for two hours at  $120^\circ$ . The tube was then opened and the contents diluted with water. The reaction had proceeded smoothly without formation of any resinous products. The solution was neutralized with caustic soda, slightly acidified with acetic acid, and extracted with ether. The ether was distilled off and the residue diluted with water, boiled with calcium carbonate, and filtered. Silver hexoate was precipitated in the filtrate by means of silver nitrate, and this compound was analyzed.

0.0630 gram gave, on ignition, 0.0300 gram Ag.

<sup>1</sup> Ann. Chem. (Liebig), 280, 263.

<sup>2</sup> Ibid., 171, 27.

<sup>3</sup> V. Meyer and Locher : Ann. Chem. (Liebig), 180, 164.

	Calculated for $C_6H_{11}COOAg$ .	Found.
Ag	48.43	47.63

*Dinitrohexane*,  $C_6H_{12}(NO_2)_2$ .

The dinitrohexane left after distilling off all nitrohexane in steam is generally impure, as it is exceedingly difficult to drive over all nitrohexane without raising the temperature so high as partially to decompose the dinitrohexane. Occasionally, when separating the spent acid from the oil, a middle layer has been noticed. When separated, washed, and dried, this was found to be pure dinitrohexane.

0.3727 gram gave 55.0 cc. nitrogen at 741 mm. and 21°.

0.1511 gram gave 0.2251 gram  $CO_2$ , and 0.0911 gram  $H_2O$ .

	Calculated for $C_6H_{12}N_2O_4$ .	Found.
C	40.90	40.65
H	6.82	6.67
N	15.91	15.94

*Properties.*—Dinitrohexane is a clear yellow oil of acid character, and of a sweet ester-like odor. It is heavier than, and somewhat soluble in, water. Readily soluble in alcohol, ether, etc. It cannot be distilled without decomposition. It is very slowly soluble in aqueous solution of sodium or potassium hydroxide, readily soluble in their alcoholic solutions with a red color.

With bromine water a heavy oily bromide is formed, which is insoluble in aqueous or alcoholic sodium hydroxide. Reduction with tin and hydrochloric acid yields ammonia as one of the products. These facts indicate that it is primary, but there was not enough at hand for more definite determinations.

*Nitroheptane*,  $C_7H_{16}NO_2$ .

The nitroheptane separated from the dinitroheptane by distillation in steam (page 211), was redistilled, the greater portion passing over at 193°–195°, without decomposition. Analysis of this fraction showed it to be pure nitroheptane.

0.1805 gram gave 16.1 cc. nitrogen at 746 mm. and 17°.

0.2253 gram gave 0.4761 gram  $CO_2$ , and 0.2043 gram  $H_2O$ .

	Calculated for $C_7H_{15}NO_2$ .	Found.
C	57.93	57.65
H	10.34	10.04
N	9.65	9.87

*Properties.*—Nitroheptane is a light-yellow oil of peculiar pleasant odor. Boiling-point  $193^{\circ}$ – $195^{\circ}$  (uncorr.); specific gravity 0.9476 at  $17^{\circ}$ . It is insoluble in water, readily soluble in alcohol, ether, etc. It is very slowly soluble in aqueous solution of sodium or potassium hydroxide, readily soluble in their alcoholic solutions. It is not explosive.

The ready volatility of all these high-boiling nitroparaffins with a low-boiling solvent is remarkable. Heptane, boiling at  $99^{\circ}$ , carries over a noticeable quantity of nitroheptane when their mixture is distilled.

*Sodium Nitroheptane*,  $C_7H_{14}NO_2Na$ .—The action of metallic sodium on nitroheptane in a solution in petroleum ether apparently produced partial decomposition. The salt was therefore prepared by sodium ethylate in solution in petroleum ether, and after washing and drying was analyzed.

0.1650 gram gave 0.0700 gram  $Na_2SO_4$ .

	Calculated for $C_7H_{14}NO_2Na$ .	Found.
Na	13.77	13.69

*Properties.*—Sodium nitroheptane is a light-yellow salt, readily soluble in water and in alcohol, insoluble in ether, petroleum ether, etc. While usually separating from all solvents as a gelatinous mass, it can with difficulty be crystallized from alcohol in fine, white needles. It blackens when heated, but is not explosive. Acids do not liberate the nitroparaffin.

With a solution of ferric chloride the characteristic intense red coloration results. The other metallic salts resemble those of nitrohexane, the mercuric derivative being yellow, the lead salt white, and the silver salt yellow, all flocculent precipitates.

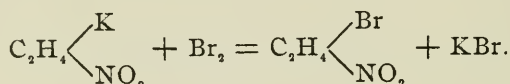
*Heptylamine*,  $C_7H_{15}NH_2$ .—The reduction of nitroheptane to the amine proceeded smoothly on gently warming with iron filings and acetic acid. The heptylamine was liberated with

caustic soda, distilled in steam, the distillate extracted with ether, and the ether removed by distillation. Part of the residual heptylamine was dissolved in hydrochloric acid and platinic chloride added. Upon concentrating and cooling, the double salt crystallized out in fine needles, and was analyzed. 0.0137 gram gave, on ignition, 0.0041 gram Pt.

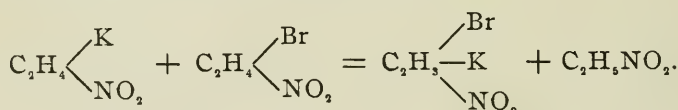
Pt	Calculated for (C <sub>7</sub> H <sub>15</sub> NH <sub>2</sub> Cl) <sub>2</sub> PtCl <sub>4</sub> .	Found.
	29.82	29.92

The heptylamine gave the isonitril reaction, showing it to be primary. The action of nitrous acid on this amine gave what was apparently an alcohol, and this product, when Liebermann's reaction was applied, gave no evidence of a secondary amine.

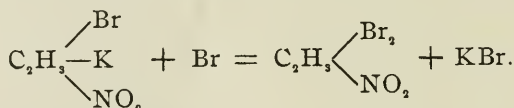
*Bromnitroheptane*, C<sub>7</sub>H<sub>14</sub>BrNO<sub>2</sub>.—V. Meyer and Tscherniak<sup>1</sup> have shown that if bromine-water is added to a solution of potassium nitroethane the following reaction takes place :



This bromnitroethane being a stronger acid than nitroethane liberates the latter from its salt, thus :



The nitroethane thus liberated is not acted upon by the bromine, but the other product reacts as follows :



Hence the final product is a mixture of mono- and dibromnitroethane, and nitroethane.

When bromine water is added to an aqueous solution of sodium nitroheptane apparently analogous reactions result, for analysis shows the product to be a mixture. Tscher-

<sup>1</sup> Ber. d. chem. Ges., 7, 732.

niak,<sup>1</sup> however, has shown that if the alkaline salt of the nitroparaffin is added to an excess of bromine water, a practically pure monobromide results, and this method gives very satisfactory results with these higher nitroparaffins.

A few grams of nitroheptane were dissolved in a little alcoholic caustic soda, and the clear solution slowly added to a large excess of bromine water. A heavy oily bromide was precipitated. The solution was made alkaline with caustic soda, and the bromide extracted with ether. The ether was removed by gentle evaporation, and the residue dried in a vacuum desiccator and analyzed.

0.2256 gram, by ignition with lime, gave 0.1801 gram AgBr.

	Calculated for $C_7H_{14}BrNO_2$ .	Found.
Br	35.71	34.02

The bromine water had been standing for some time and contained some hydrobromic acid which apparently liberated some nitroheptane, thus accounting for the somewhat low percentage of bromine.

*Properties.*—Bromnitroheptane is an almost colorless oil with a penetrating odor, affecting the eyes. It is insoluble in and heavier than water, soluble in alcohol, ether, etc., slowly soluble in concentrated aqueous solution of caustic soda; rather readily soluble in alcoholic caustic soda. It could not be solidified by a freezing-mixture of snow and salt. From the method of its preparation and its solubility in alka-

lies, its structure follows as  $C_6H_{13}-\begin{array}{c} \text{H} \\ \diagup \\ \text{C}-\text{Br} \\ \diagdown \\ \text{NO}_2 \end{array}$ .

*Heptylnitrolic Acid*,  $C_7H_{14}N_2O_3$ .—A small quantity of nitroheptane was dissolved in alcoholic caustic potash, potassium nitrite added, the solution well cooled, and treated successively with excess of dilute sulphuric acid and of caustic potash. The red coloration due to the formation of the nitrolic acid appeared each time with excess of alkali. The process was twice repeated, then the slightly acid solution extracted with ether, and the ether removed from the extract by spon-

<sup>1</sup> Ann. Chem. (Liebig), 180, 126.

taneous evaporation. The residual nitrolic acid was a clear yellow liquid of sweet odor. It was converted into the fatty acid by digestion with dilute sulphuric acid<sup>1</sup> and the silver salt of the latter formed and analyzed.

0.0512 gram gave, on ignition, 0.0231 gram Ag.

	Calculated for $C_6H_{13}COOAg$ .	Found.
Ag	45.57	45.30

*Action of Hydrochloric Acid.*—As a primary nitroparaffin, nitroheptane, when heated with concentrated hydrochloric acid, should yield heptonic acid and hydroxylamine, and this was found to be the case. About 5 grams of nitroheptane were heated in a sealed tube with 10 grams of concentrated hydrochloric acid for two hours at 125°. The reaction proceeded smoothly without the formation of a trace of resinous products. The tube was opened and the fatty acid converted into the silver salt in the manner described under hexane. This silver salt was analyzed.

0.0256 gram gave, on ignition, 0.0116 gram Ag.

	Calculated for $C_6H_{13}COOAg$ .	Found.
Ag	45.57	45.33

After removal of the fatty acid, the residual solution reduced Fehling's solution, showing the presence of hydroxylamine.

*Dinitroheptane,  $C_7H_{14}(NO_2)_2$ .*

The residue left after distilling off nitroheptane in steam from the mixed nitro-products is generally impure for the reason mentioned under dinitrohexane. Dinitroheptane is best obtained by the action of mixed sulphuric acid and nitric acid (of sp. gr. 1.42) on heptane when it usually partially separates as a middle layer, which may easily be purified by washing. Analysis of the compound thus obtained gave the following results:

0.1421 gram gave 18.4 cc. nitrogen at 738 mm. and 20°.

0.3317 gram gave 0.5407 gram  $CO_2$ , and 0.2011 gram  $H_2O$ .

<sup>1</sup> V. Meyer: Ann. Chem. (Liebig), **175**, 108.



	Calculated for $C_7H_{14}N_2O_4$ .	Found.
C	44.21	44.45
H	7.37	7.08
N	14.74	14.37

*Properties.*—Dinitroheptane is a clear, yellow oil of pleasant ester-like odor, sparingly soluble in water, readily soluble in alcohol, ether, etc. It carbonizes on heating but is not explosive. It is very slowly soluble in aqueous solution of caustic soda, readily soluble in its alcoholic solution, with a red color.

*Sodium Dinitroheptane*,  $C_7H_{13}(NO_2)_2Na$ .—The sodium salt was precipitated by a solution of sodium ethylate in petroleum ether. The gelatinous mass thus obtained retained sodium ethylate with great persistency, and could not be obtained quite pure.

0.0941 gram gave 0.0371 gram  $Na_2SO_4$ .

	Calculated for $C_7H_{13}(NO_2)_2Na$ .	Found.
Na	10.85	12.7

*Properties.*—Sodium dinitroheptane, when dry, is a yellow powder, turning red on exposure to light. It is readily soluble in water and alcohol, insoluble in ether, petroleum ether, etc. It could not be crystallized from any solvent. It always separates as a gelatinous mass. It blackens when heated, but is not explosive.

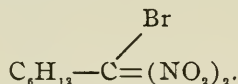
Addition of mercuric chloride to a solution of sodium dinitroheptane gives a yellow precipitate. The silver salt is yellow, rapidly darkening, and the lead salt is white. Ferric chloride in the cold gives immediately a red-brown precipitate.

*Bromdinitroheptane*,  $C_7H_{13}Br(NO_2)_2$ .—When a solution of sodium dinitroheptane was added to an excess of bromine water, a heavy oily bromide resulted. The solution was made alkaline with caustic soda and the bromide extracted with ether, the ether being then removed from the extract by gentle evaporation. The residual bromide was dried in a vacuum desiccator and analyzed.

0.2577 gram gave, by ignition with lime, 0.1790 gram AgBr.

	Calculated for $C_7H_{13}Br(NO_2)_2$ .	Found.
Br	29.74	29.52

*Properties.*—Bromdinitroheptane is a light-yellow liquid of penetrating odor, affecting the eyes. Insoluble in, and heavier than, water. It is soluble in alcohol, ether, etc., insoluble in aqueous or alcoholic solution of caustic soda. Its structure must be represented by the formula,



*Reduction of Dinitroheptane.*—When dinitroheptane was reduced with tin and hydrochloric acid the products were ammonia, hydroxylamine, and a neutral product, probably an aldehyde. Hydroxylamine was shown to be present by the reducing action of the solution on Fehling's solution. The ammonia was distilled off in steam from the alkaline liquid and the chlorplatinate formed.

0.3735 gram gave 0.1617 gram Pt.

	Calculated for $(NH_4Cl)_2PtCl_4$ .	Found.
Pt	43.92	43.30

*Nitrooctane*,  $C_8H_{17}NO_2$ .

The nitrooctane obtained by distilling the mixed nitro-compounds in steam (page 211) was dried and fractioned. It distilled chiefly between  $206^\circ$  and  $210^\circ$  with some decomposition.<sup>1</sup> This fraction was analyzed.

0.2523 gram gave 19.0 cc. nitrogen at  $17^\circ$  and 755 mm.

0.1334 gram gave 0.2968 gram  $CO_2$ , and 0.1242 gram  $H_2O$ .

	Calculated for $C_8H_{17}NO_2$ .	Found.
C	60.37	60.64
H	10.69	10.35
N	8.83	8.64

*Properties.*—Nitrooctane is a light-yellow oil of pleasant ethereal odor. It boils at  $206^\circ$ – $210^\circ$  with some decomposition. Its specific gravity is 0.9346 at  $20^\circ$ . It is soluble in alcohol, ether, and other organic solvents, insoluble in water,

<sup>1</sup> Cf. Eichler : Ber. d. chem. Ges., 12, 1883.

very slowly soluble in aqueous solutions of caustic soda or caustic potash, readily soluble in their alcoholic solutions. Upon long standing the color turns to a red.

*Sodium Nitrooctane*,  $C_8H_{16}NO_2Na$ .—The sodium salt was prepared by means of a solution of sodium ethylate in petroleum ether in the manner previously described. The dried salt was analyzed.

0.1920 gram gave 0.0760 gram  $Na_2SO_4$ .

	Calculated for $C_8H_{16}NO_2Na$ .	Found.
Na	12.70	12.76

*Properties*.—Sodium nitrooctane, when dry, is a yellow powder, readily soluble in water and in alcohol, insoluble in ether, petroleum ether, etc. It could not be crystallized, separating from all solvents as a gelatinous mass. Eichler<sup>1</sup> obtained the same result. It blackens when heated, but is not explosive. With ferric chloride the characteristic intense red coloration results. The other metallic derivatives resemble those of nitroheptane.

*Octylamine*,  $C_8H_{17}NH_2$ .—The reduction of nitrooctane to the amine was carried out with iron filings and dilute acetic acid. A primary amine resulted, giving the isonitril reaction. The chlorplatinate was formed by adding platinic chloride to the solution of the amine in hydrochloric acid. Upon concentrating and cooling, the chlorplatinate separated in fine yellow needles. Analysis of this double salt gave the following result :

0.1167 gram gave, by ignition, 0.0342 gram Pt.

	Calculated for $(C_8H_{17}NH_2Cl)_2PtCl_4$ .	Found.
Pt	29.20	29.32

*Bromnitrooctane*,  $C_8H_{16}BrNO_2$ .—When sodium nitrooctane was dissolved in water and the solution treated with bromine water in excess, a heavy oil separated. This was washed with caustic soda, dried, and analyzed.

0.1224 gram gave, by ignition with lime, 0.0764 gram AgBr.

<sup>1</sup> *Loc. cit.*

	Calculated for $C_8H_{16}BrNO_2$ .	Found.
Br	33.62	26.64

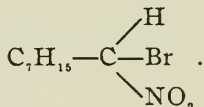
As shown before, under nitroheptane, this product was doubtless a mixture of nitrooctane, bromnitrooctane, and dibromnitrooctane.

When the solution of sodium nitrooctane was added to an excess of bromine water, however, the pure bromide was obtained. The heavy oil was washed with dilute caustic soda, extracted with ether, and the ether removed by evaporation. The residual bromide was dried in a vacuum desiccator and analyzed.

0.1730 gram gave, by ignition with lime, 0.1371 gram AgBr.

	Calculated for $C_8H_{16}BrNO_2$ .	Found.
Br	33.62	33.53

*Properties.*—Bromnitrooctane is a yellow liquid, heavier than water. It is insoluble in water, soluble in alcohol, ether, etc., slowly soluble in concentrated aqueous solution of sodium or potassium hydroxides, readily soluble in their alcoholic solutions. It has a penetrating disagreeable odor, cannot be distilled without decomposition, and cannot be solidified by a freezing-mixture of snow and salt. Its structure follows from the method of its preparation and its properties as



*Octylnitrolic Acid*,  $C_8H_{16}N_2O_3$ .—About 10 grams of nitrooctane were dissolved in alcoholic caustic potash, potassium nitrite added, and the well-cooled solution slowly acidified with dilute sulphuric acid. With excess of caustic potash the red coloration due to a nitrolic acid appeared. The process was twice repeated, then the slightly acid solution was extracted with ether, and the ether removed from the extract by spontaneous evaporation, leaving the nitrolic acid as a light-yellow liquid of sweet odor.<sup>1</sup>

<sup>1</sup> Cf. Eichler: *Loc. cit.*

The nitrolic acid was converted into the fatty acid by digesting with dilute sulphuric acid. The fatty acid was extracted with ether, and the silver salt formed and analyzed.

0.1440 gram gave, on ignition, 0.0620 gram Ag.

	Calculated for $C_7H_{15}COOAg$ .	Found.
Ag	43.07	43.10

*Action of Hydrochloric Acid.*—As a primary nitroparaffin, nitrooctane should, when heated with concentrated hydrochloric acid, yield octoic acid and hydroxylamine. About 5 grams of nitrooctane were heated in a sealed tube with 10 grams concentrated hydrochloric acid for two hours at  $125^\circ$ . Upon cooling and opening the tube no pressure was observed nor was there any resinous matter, indicative of secondary nitroparaffins. The fatty acid, present in large quantity, was converted into the silver salt in the way previously described, and the latter analyzed.

0.0412 gram gave, on ignition, 0.0180 gram Ag.

	Calculated for $C_7H_{15}COOAg$ .	Found.
Ag	43.07	43.66

*Dinitrooctane,  $C_8H_{16}(NO_2)_2$ .*

The residue left after distilling off all nitrooctane in steam was found to be impure, as it is exceedingly difficult to drive over all nitrooctane without raising the temperature so high as partially to decompose the dinitrooctane. The latter is best obtained pure by the action of mixed sulphuric acid and nitric acid (sp. gr. 1.42) upon octane, when, on cooling, it partially separates as a middle layer.

Analysis of dinitrooctane obtained by the latter method gave the following results :

0.3964 gram gave 46.0 cc. nitrogen at 750 mm. and  $15^\circ$  C.  
0.4884 gram gave 0.8469 gram  $CO_2$ , and 0.3559 gram  $H_2O$ .

	Calculated for $C_8H_{16}N_2O_4$ .	Found.
C	47.06	47.27
H	7.84	8.08
N	13.73	13.63

*Properties.*—Dinitrooctane is a clear, yellow liquid which easily decomposes on heating. Its specific gravity is 1.0638 at 23°. It is soluble in alcohol, ether, etc., sparingly soluble in water. With alkalis either in aqueous or alcoholic solution it gives an intense red color. It could not be solidified by snow and salt.

*Sodium Dinitrooctane*,  $C_8H_{15}(NO_2)_2Na$ .—The sodium salt as obtained by precipitation with a solution of sodium ethylate in petroleum ether, retained sodium ethylate even after repeated washing with hot petroleum ether.

0.2432 gram gave 0.0816 gram  $Na_2SO_4$ .

	Calculated for $C_8H_{15}N_2O_4Na$ .	Found.
Na	10.20	11.70

*Properties.*—Sodium dinitrooctane is a red salt, soluble in alcohol and water. It could not be crystallized. It resembled the corresponding salt of dinitroheptane.

*Bromdinitrooctane.*—When sodium dinitrooctane is added to an excess of bromine water, a heavy oily bromide separates which is insoluble in aqueous or alcoholic caustic soda. Its

formula is doubtless  $C_7H_{15}C \begin{smallmatrix} Br \\ \diagup \\ \diagdown \\ (NO_2)_2 \end{smallmatrix}$ , but it was not analyzed.

*Reduction of Dinitrooctane.*—When reduced with tin and hydrochloric acid, dinitrooctane yielded ammonia, hydroxylamine, and octoic acid as would be expected in the case of a primary dinitroparaffin.

The fatty acid formed was separated by distillation in steam, and the silver salt formed in the usual way and analyzed.

0.1360 gram gave 0.0785 gram  $AgCl$ .

	Calculated for $C_7H_{15}COOAg$ .	Found.
Ag	43.07	43.38

The residual acid solution when made alkaline with caustic soda reduced Fehling's solution showing the presence of hydroxylamine. The ammonia was separated by distilling in steam, and converted into the chlorplatinate. Analysis of the latter gave the following result :

0.4885 gram gave 0.2137 gram Pt.



	Calculated for (NH <sub>4</sub> Cl) <sub>2</sub> PtCl <sub>4</sub> .	Found.
Pt	43.92	43.75

*Nitrononane*, C<sub>9</sub>H<sub>19</sub>NO<sub>2</sub>.

The distillate obtained from the mixed nitro-compounds by steam was redistilled in steam, the first portion of the distillate being rejected as possibly containin gnonane. Nitrononane completely decomposes when distilled under atmospheric pressure, but as above obtained it was a clear, light-yellow liquid, which analysis showed to be pure.

0.3164 gram gave 24.0 cc. nitrogen at 747 mm. and 17°.

0.2223 gram gave 0.5092 gram CO<sub>2</sub>, and 0.2185 gram H<sub>2</sub>O.

	Calculated for C <sub>9</sub> H <sub>19</sub> NO <sub>2</sub> .	Found.
C	62.42	62.48
H	10.98	10.92
N	8.09	8.34

*Properties.*—Nitrononane is a light-yellow liquid of pleasant ester-like odor, boiling at 215°–218° with considerable decomposition, but volatile with steam. Its specific gravity is 0.9227 at 17°. Like the other nitroparaffins of high molecular weight it is insoluble in water, and practically insoluble in aqueous solution of caustic soda. It is readily soluble in alcohol, ether, etc., and in alcoholic caustic soda. It could not be solidified by a freezing-mixture of snow and salt, and was not explosive.

*Sodium Nitrononane*, C<sub>9</sub>H<sub>18</sub>NO<sub>2</sub>Na.—The sodium salt was prepared by precipitation with sodium ethylate in petroleum ether solution. It retained sodium ethylate with persistency and was not obtained pure.

0.0765 gram gave 0.0332 gram Na<sub>2</sub>SO<sub>4</sub>.

	Calculated for C <sub>9</sub> H <sub>18</sub> NO <sub>2</sub> Na.	Found.
Na	11.78	13.90

*Properties.*—The precipitated sodium salt as above obtained was a yellow, gelatinous mass which could not be crystallized. It was readily soluble in water and alcohol, gave the intense red coloration with ferric chloride, and blackened upon heating, but was not explosive.

*Bromnitrononane*,  $C_9H_{18}BrNO_2$ .—When bromine water was added to an aqueous solution of sodium nitrononane, apparently analogous reactions to those described by Meyer and Tscherniak<sup>1</sup> took place. A heavy oil was precipitated which was washed with caustic soda, dried, and analyzed.

0.2356 gram gave, by ignition with lime, 0.0785 gram AgBr.

	Calculated for $C_9H_{18}BrNO_2$ .	Found.
Br	31.7	14.2

When the sodium salt was added to an excess of bromine water, however, the pure bromide was obtained. The oil thus formed was washed with caustic soda, dried in a vacuum-desiccator, and analyzed.

0.3064 gram gave 0.2270 gram AgBr.

	Calculated for $C_9H_{18}BrNO_2$ .	Found.
Br	31.74	31.48

*Properties*.—Bromnitrononane is a clear, yellow liquid, slowly soluble in caustic potash. With sodium ethylate in solution in petroleum ether a sodium salt was precipitated. It has the characteristic, penetrating odor noticed in the case of the other bromides.

*Nonylamine*,  $C_9H_{19}NH_2$ .—A few grams of nitrononane were reduced to the amine by warming gently with iron filings and dilute acetic acid. The amine was liberated by caustic soda and distilled in steam. It gave the isonitril reaction, and with sodium nitroprusside and acetone it gave the deep-violet coloration recently shown by Rimini<sup>2</sup> to be characteristic only of primary amines.

The addition of platinic chloride to the solution of the amine in hydrochloric acid gave no precipitate, but upon concentrating and cooling, the double salt crystallized out in golden-yellow needles. These were dried and analyzed.

0.1472 gram gave, on ignition, 0.0417 gram Pt.

	Required for $(C_9H_{19}(NH_2Cl))_2PtCl_4$ .	Found.
Pt	28.02	28.33

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Chem. Centrbl., 1898, 2, [2], 132.

*Nonylnitrolic Acid*,  $C_9H_{18}N_2O_5$ .—About 5 grams of nitrononane were dissolved in alcoholic caustic soda, sodium nitrite added, and the well-cooled solution slowly acidified with dilute sulphuric acid. Upon adding excess of alcoholic caustic soda again only a faint red color resulted. The process was twice repeated, then the faintly acid solution extracted with ether, and the ether removed from the extract by spontaneous evaporation.

By digesting with dilute sulphuric acid the yellow liquid left, it was shown to contain at least some nitrolic acid. A fatty acid was formed whose silver salt was analyzed.

0.1930 gram gave 0.0763 gram Ag.

	Calculated for $C_8H_{17}COOAg$ .	Found.
Ag	40.75	39.55

*Action of Hydrochloric Acid*.—About 5 grams of nitrononane were heated in a sealed tube with 10 grams of concentrated hydrochloric acid for two hours at  $120^\circ$ . The reaction proceeded smoothly without the formation of resinous products, and the fatty acid was present in large quantity. The silver salt of the latter was analyzed.

0.2032 gram gave, on ignition, 0.0799 gram Ag.

	Calculated for $C_8H_{17}COOAg$ .	Found.
Ag	40.75	39.32

After extracting the nonoic acid, the hydrochloric acid solution, when made alkaline with caustic soda, reduced Fehling's solution and gave off ammonia, thus showing the presence of hydroxylamine.

*Dinitrononane*,  $C_9H_{18}(NO_2)_2$ .—The residue left after distilling off nitrononane in steam from the mixed nitro-products of nonane had partially decomposed during distillation. Several nitrogen determinations gave a mean of 10.02 per cent in place of 12.84 per cent required by theory. But while the dinitroparaffin itself was impure, certain derivatives could be prepared from it in a pure state.

*Sodium Dinitrononane*,  $C_9H_{17}N_2O_4Na$ .—The sodium salt was

prepared by precipitation with sodium ethylate in solution in petroleum ether.

0.2198 gram gave 0.0680 gram  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{C}_9\text{H}_{17}\text{N}_2\text{O}_4\text{Na}$ .	Found.
Na	9.59	10.05

*Properties.*—Sodium dinitrononane resembled the corresponding derivative of dinitrooctane. It was yellowish-red, soluble in water and alcohol, and was deposited from either solvent as a gelatinous mass that could not be crystallized.

*Bromdinitrononane*,  $\text{C}_9\text{H}_{17}\text{BrN}_2\text{O}_4$ .—When a solution of sodium dinitrononane was added to an excess of bromine water, a heavy oily bromide was precipitated. The solution was made alkaline with caustic soda, and the bromide extracted with ether. The ether was removed by gentle evaporation.

0.3123 gram, by ignition with lime, gave 0.1936 gram  $\text{AgBr}$ .

	Calculated for $\text{C}_9\text{H}_{17}\text{BrN}_2\text{O}_4$ .	Found.
Br	26.9	26.6

*Properties.*—Bromdinitrononane is a heavy, yellow liquid, insoluble in water, soluble in alcohol, ether, etc., insoluble in concentrated aqueous or alcoholic caustic soda. It could not be solidified by snow and salt.

*Reduction of Dinitrononane.*—A small quantity of dinitrononane was reduced with iron filings and acetic acid, the mixture being gently warmed. The acid solution was partially neutralized with caustic soda, then extracted with ether, and the ether evaporated from the extract. The residual fatty acid was boiled with calcium carbonate, and filtered. The silver salt was precipitated from the filtrate, washed, dried, and analyzed.

0.0778 gram gave 0.0320 gram  $\text{Ag}$ .

	Calculated for $\text{C}_8\text{H}_{17}\text{COOAg}$ .	Found.
Ag	40.75	41.13

The other product of the reaction was ammonia.

*Nitrodecane*,  $C_{10}H_{21}NO_2$ .

The distillate obtained by steam from the mixed nitro-products of decane was again distilled in steam, dried, and analyzed.

0.1404 gram gave 0.3313 gram  $CO_2$ , and 0.1399 gram  $H_2O$ .

	Calculated for $C_{10}H_{21}NO_2$ .	Found.
C	64.17	64.35
H	11.23	11.07

*Properties.*—Nitrodecane is a clear, yellow liquid with the peculiar sweet odor characteristic of these higher nitroparaffins. Its specific gravity is 0.9105 at  $15^\circ$ .<sup>1</sup> It cannot be distilled without decomposition, but is volatile with steam. It is readily miscible with alcohol, ether, etc., soluble in alcoholic caustic potash. The nitrolic-acid test resulted in an orange-red coloration, and the sodium salt gave a brown precipitate with ferric chloride.

*Nitrohendecane*,  $C_{11}H_{23}NO_2$ .

Nitrohendecane was separated from the dinitroparaffin by two distillations in steam. Analysis showed it to be pure.

0.1731 gram gave 0.4200 gram  $CO_2$ , and 0.1776 gram  $H_2O$ .

	Calculated for $C_{11}H_{23}NO_2$ .	Found.
C	65.67	65.42
H	11.44	11.36

*Properties.*—The nitrohendecane is a clear, yellow liquid of specific gravity 0.9001 at  $15^\circ$ . It cannot be distilled without decomposition but is volatile with steam. It is readily miscible with alcohol and ether, insoluble in water. The nitrolic-acid test resulted in an orange-yellow coloration.

*Nitrododecane*,  $C_{12}H_{25}NO_2$ .

The nitrododecane obtained by two distillations in steam still contained traces of the free hydrocarbon, analyses showing both carbon and hydrogen too high. The quantity at hand was too small to admit of purification. The nitrododec-

<sup>1</sup> The specific gravity determination of this and the two higher nitroparaffins were necessarily carried out with small quantities of material. But it is believed that the figures given are fairly accurate.

ane resembled the preceding nitroparaffin, the nitrolic-acid test resulting in a yellow coloration.

An investigation of certain other derivatives and reactions of these higher nitroparaffins is now in progress.

LAFAYETTE, IND., Dec., 1898.

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## THE ACTION OF ETHYLIC OXALATE ON CAMPHOR. (IV).

BY J. BISHOP TINGLE AND ALFRED TINGLE.

### *Theoretical.*

In the previous papers on this subject<sup>1</sup> Bishop Tingle has described the method employed for the preparation of camphoroxalic acid. We have now succeeded in improving and simplifying the process by hydrolyzing the mixture of borneol, camphor, and ethylic camphoroxalate together in one operation, so that the preparation and purification of the compound need only occupy a few hours distributed over three days.

According to the experimental conditions, three compounds are formed by the interaction of aniline and camphoroxalic acid. For the sake of convenience we will describe the preparation and chief properties of them all before discussing their constitution. When aniline (2 mols.) and camphoroxalic acid (1 mol.) are heated together at 130° a compound,  $C_{17}H_{21}NO$ , is formed which crystallizes in colorless, rhombic plates, and occasionally in slender, hair-like needles, upwards of an inch in length. It is readily soluble in benzene or ethylic acetate, but only sparingly so in light petroleum, and melts at 166°. It does not react with ferric chloride; bromine causes the production of a hydrobromide, whilst hydroaurochloric acid and hydroplatinochloric acid yield the corresponding salts, of which the former is very unstable. Prolonged boiling with concentrated alkali is without appreciable effect on the base. The second compound is formed by mixing concentrated benzene solutions of aniline (2 mols.) and camphoroxalic acid (1 mol.), and warming the liquid for a few moments on the water-bath. The compound crystallizes from

<sup>1</sup> This JOURNAL, 20, 318 (1898); *Ibid.*, 19, 393 (1897); J. Chem. Soc., 57, 652 (1890).

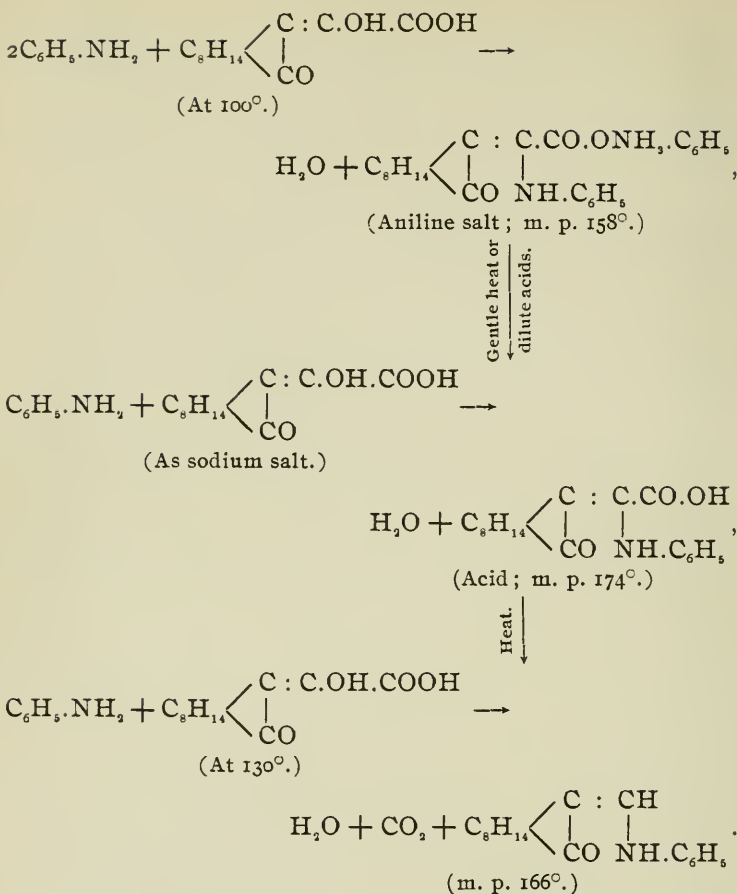


a mixture of benzene and light petroleum in small, colorless needles, which melt and decompose at  $158^{\circ}$ . The substance is an aniline salt and has the formula  $C_{24}H_{28}N_2O_3$ . When slowly heated below its melting-point, it gives up aniline and yields the third compound described below. If quickly heated above its melting-point, it yields aniline, carbon dioxide, and the substance (m. p.  $166^{\circ}$ ) already described. In the absence of moisture and acid vapors this aniline salt is stable, but it is slowly hydrolyzed on warming with water or alcohol; alkalis decompose it much more rapidly, and in two stages: in the first stage the alkali salt of the corresponding acid is produced, with liberation of aniline; in the second stage this salt is broken down as described later.

By the action of dilute (1 : 6) sulphuric acid, or hydrochloric acid, at the ordinary temperature the aniline salt suffers immediate decomposition, aniline is eliminated, and a yellow acid,  $C_{18}H_{21}NO_3$ , is formed which is insoluble in water. It is deposited from a mixture of benzene and light petroleum in bright yellow needles, and melts and decomposes at  $174^{\circ}$ .

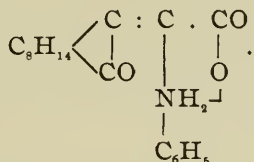
The third compound which we have obtained from aniline and camphoroxalic acid is identical with the foregoing substance, and is also prepared by boiling aniline with sodium camphoroxalate, in equimolecular proportion, in dilute alcoholic solution. The compound has well-developed acidic properties, and liberates carbonic anhydride from an aqueous solution of sodium carbonate; the sodium salt is practically colorless. Prolonged boiling with concentrated alcoholic potash or soda causes a slow decomposition of the compound into aniline and camphoroxalic acid. When heated above its melting-point alone, or at  $140^{\circ}$  in the presence of ethylaniline, carbonic anhydride is evolved, and the compound first described (m. p.  $166^{\circ}$ ) is produced.

For convenience we give a diagrammatic representation of the modes of formation and interrelationship of the foregoing compounds and of the formulæ which we assign to them:

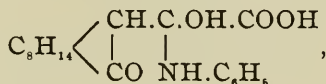


Various names suggest themselves for the compounds; we believe the simplest plan to adopt is to regard them as being derived from the complex  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} : \text{CH}_2 \\ | \\ \text{CO} \end{array}$  for which the term camphoformene may be employed. It is self-explanatory, and indicates the presence of the double linkage. The first of the above compounds is then aniline phenylcamphoformeneamine carboxylate; the second, phenylcamphoformeneaminecarboxylic acid; whilst the third is phenylcam-

phoformeneamine. The pronounced yellow color of the carboxylic acid, and its absence from the aniline and sodium salts makes it probable that there is a more intimate linkage in the first than in the others, so that the free acid should possibly be represented by the "betaine" formula,



We have not observed any similar recorded instance of the action of aniline on an unsaturated hydroxy acid, and we believe that the formation of phenylcamphoformeneaminecarboxylic acid from sodium camphoroxalate under the conditions described is noteworthy. Probably the first product in this, as in the experiments resulting in the formation of the other compounds, is a purely additive one; *viz.*,



which must be highly unstable, as we have hitherto failed to isolate it. By loss of the elements of water it then passes into the unsaturated carboxylic acid. This view of the reaction brings it into harmony with that of hydroxylamine and sodium camphoroxalate, which, as Bishop Tingle<sup>1</sup> has shown,

yield the additive compound,  $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{CH} \cdot \text{C} \cdot \text{OH} \cdot \text{CO} \cdot \text{OH} \\ \diagdown \text{CO} \end{array} \begin{array}{l} | \\ \text{NH} \cdot \text{OH} \end{array}$ .

This substance is quite stable, and can, without difficulty, be

converted into the isoxazole,  $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} \cdot \text{CH} \\ \diagdown \text{C} \end{array} \begin{array}{l} || \\ \text{N} \end{array} \begin{array}{l} || \\ \text{O} \end{array}$ , with loss of

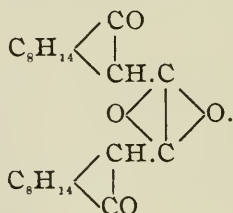
2 molecules of water, a reaction analogous, to some extent, with that leading to the formation of the above phenylcamphoformeneamine. On account of this analogy the possible alterna-

<sup>1</sup> This JOURNAL, 19, 393 (1897).

tive formula  $C_8H_{14} \begin{array}{l} \diagup C \text{---} CH.CO.OH \\ | \quad \diagdown \\ CO \quad N.C_6H_5 \end{array}$  for the carboxylic

acid suggests itself. At present we believe that the properties of the compound and the conditions under which it is formed are not such as to justify the assumption of the production of a closed chain, even apart from the question of analogy. Subsequently to Bishop Tingle's work just referred to C. Harries<sup>1</sup> and his colleagues showed that hydroxylamine also forms additive compounds with various unsaturated ketones such as phorone.

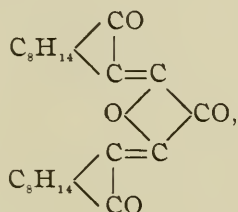
In addition to acetylcamphoroxalic acid (m. p.  $133^\circ.5$ – $134^\circ.5$ ), Bishop Tingle<sup>2</sup> has described two other compounds formed by the action of acetic anhydride on camphoroxalic acid, which melt at  $190^\circ$ – $191^\circ$  and  $242^\circ$ – $242^\circ.5$ , respectively. We have prepared the former in somewhat larger quantity by boiling camphoroxalic acid with benzoyl chloride. The compound crystallizes from a mixture of benzene and light petroleum in minute colorless needles; it is not changed by boiling with sodium hydrate solution, nor does it combine with bromine in chloroform solution; hydroxylamine is also without action on the substance. Analyses and molecular weight determinations by the cryoscopic method lead to the formula  $C_{22}H_{30}O_4$ . The compound is evidently not an anhydride as was at first suggested; we believe that it may be best represented, at least provisionally, by the formula



The high-melting compound referred to above has also been obtained in somewhat larger quantity by boiling acetic anhydride with camphoroxalic acid. Its production appears to be dependent on the strict purity of the anhydride and the dura-

<sup>1</sup> Ber. d. chem. Ges., 30, 231 et seq.    <sup>2</sup> This JOURNAL, 20, 324 (1898).

tion of the heating. With inferior specimens of anhydride none of the compound is formed; boiling during periods much less than two hours gives rise to uncrystallizable resinous substances, whilst camphor is the chief product if the heating is prolonged much beyond that time. These observations explain the difficulties previously encountered in the preparation of this body. The compound does not react with alcohol and ferric chloride, nor with bromine in chloroform solution; with aqueous sodium hydrate a portion dissolves and the remainder acquires a yellow color. Analysis leads to the empirical formula  $C_{22}H_{28}O_4$ ; graphically we may represent the compound as



which is in harmony with the little we know of it.

Professor Carter has communicated to us the result of an additional experiment on the physiological action of camphoroxalic acid. He finds that when injected intravenously, to the extent of 0.241 gram per kilo of body weight, it is practically without effect. The results previously obtained<sup>1</sup> therefore require correction.

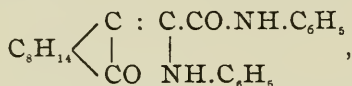
The good yield of ethylic camphoroxalate obtained from the acid by E. Fischer's method led us to determine the effect of the duration of the time of heating. We find that the yield is practically the same whether the acid is boiled during seven and three-fourths hours or during thirteen hours. In Fischer and Speier's experiments<sup>2</sup> absolute alcohol was exclusively employed. As this is not always readily available, it occurred to us to try the effect of 90 per cent. alcohol, together with a larger quantity of sulphuric acid (7 per cent. by volume). The yield, after boiling during eleven and a half hours, was 93.3 per cent of the camphoroxalic acid employed. We hope that

<sup>1</sup> This JOURNAL, 20, 342 (1898).

<sup>2</sup> Ber. d. chem. Ges., 28, 3252.

this modification of the original method may find a useful and wider application.

When ethylic camphoroxalate is heated at 130° with aniline, water and alcohol are eliminated and phenylcamphorformeneaminecarboxylic anilide,



is produced. It crystallizes from a mixture of benzene and light petroleum in small, colorless needles, melting at 193°. The compound is not changed by bromine in chloroform solution, nor by prolonged boiling with alcoholic or aqueous soda. Treatment with sulphuric acid readily gives rise to resinous products. An unstable platinochloride appears to be formed, but auric chloride in dilute hydrochloric acid solution quickly undergoes reduction.

We desire to take this opportunity of correcting an error in Bishop Tingle's first paper on this subject<sup>1</sup> in which it is stated that aniline and ethylic camphoroxalate yield oxanilide. At that time pure ethylic oxalate had not been prepared, and the mistake arose from the use of the crude compound containing ethylic oxalate in much larger proportion than was suspected. Unfortunately the erroneous statement has been copied into Morley & Muir's edition of "Watts' Dictionary of Chemistry."

In continuation of experiments previously recorded,<sup>2</sup> we attempted to isolate the oxidation-product of ethylic camphoroxalate phenylhydrazide. Mercuric oxide does not appear to be a suitable reagent to employ for its production, but good results were obtained by the use of hydrogen peroxide in ethereal solution at the ordinary temperature. The resulting ethylic camphor oxalate azobenzene,  $\text{C}_8\text{H}_{14} \begin{cases} \text{C} : \text{C.CO.OC}_6\text{H}_5 \\ | \quad | \\ \text{CO} \quad \text{N} : \text{N.C}_6\text{H}_5 \end{cases}$ , crystallizes

from a mixture of ethylic acetate and light petroleum in red needles, melting at 210°. It is much more readily soluble in ether than the phenylhydrazide, and is only slowly attacked by glacial acetic acid.

<sup>1</sup> J. Chem. Soc., 57, 655 (1890).

<sup>2</sup> This JOURNAL, 20, 338 (1893).



An unsuccessful attempt was made to prepare isoamylic camphoroxalate by boiling the acid with excess of isoamylic alcohol containing 4.57 per cent of hydrogen chloride. The product ultimately obtained could not be induced to crystallize, owing to the presence of impurities of high boiling-point. These were probably chlorine derivatives, originating from the action of hydrogen chloride on the isoamylic alcohol. It would be interesting to investigate whether any modification of Fischer's method of etherification could be devised which would permit its use for the preparation of the ethereal salts of the higher aliphatic alcohols.

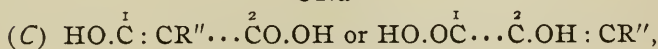
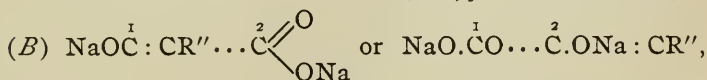
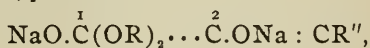
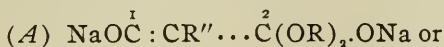
In a discussion of the formation of camphoroxalic acid<sup>1</sup> an explanation was suggested based on Claisen's theory of the interaction of ketones,  $R.CO.CH_2X$ , and ethereal salts. The hypothesis given involves the successive production of the hypothetical compounds  $NaO.C(OR)_2.C(OR)_2.ONa$  and

$C_8H_{14} \begin{matrix} \swarrow CO \\ | \\ C : C.ONa.C(OR)_2.ONa \end{matrix}$  before the treatment with

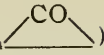
water, and of the compound  $C_8H_{14} \begin{matrix} \swarrow CO \\ | \\ C : C.ONa.CO.ONa \end{matrix}$

afterwards ( $R=C_2H_5$  or  $C_{10}H_{18}$ ). Should this explanation be valid, then, apart from possible stereoisomers, only one acid can be produced from camphor and ethylic oxalate on account of the molecular symmetry of the latter, but if an unsymmetrical dibasic acid were employed two structurally different acids might be obtained according to which of the original carbethoxyl groups reacted with the camphor, thus :

The first additive compound  $NaO.\overset{1}{C}(OR)_2 \dots \overset{2}{C}(OR)_2.ONa$ , would become successively



<sup>1</sup> This JOURNAL, 19, 407 (1897).

( $R = C_2H_5$  or  $C_{10}H_{16}$ ;  $R'' = C_8H_{14}$  ). The original carboxyl carbon atoms have been numbered 1 and 2 for the sake of clearness. Pyrotartaric acid,  $CH_3 \cdot CH \cdot CH_2 \cdot COOH$ ,  
 $\quad \quad \quad |$   
 $\quad \quad \quad COOH$

is perhaps the simplest acid fulfilling the conditions necessary to test this hypothesis, and our first experiments on the lines indicated were made with it. Diethylic pyrotartrate is readily prepared by Fischer's method, and the yield is very good.

Sodium wire only dissolves slowly in a light petroleum solution of camphor and ethylic pyrotartrate. The product, treated in the manner previously described for camphor and ethylic oxalate, yields a condensation-compound which gives a red coloration with ferric chloride and alcohol. Attempts to hydrolyze it were unsuccessful; the acid is evidently much less stable toward alkalis than camphoroxalic acid, and, under the conditions we employed, was resolved into its constituents. The yield of condensation-product was somewhat small, and we endeavored to increase it by varying the experimental conditions, but, hitherto, without success.

In the hope that a more favorable result might be obtained with oxalacetic acid, which is also an unsymmetrical dibasic acid, we investigated the interaction of camphor and ethylic oxalacetate in presence of sodium. The resulting product is a syrup, which, in aqueous solution, acquires a blue-purple color on the addition of dilute mineral acids in not too great excess. In ethereal solution the compound is yellowish-brown. With aqueous alkali a deep-red coloration is produced which changes to the blue on the addition of a little acid, but disappears when a large excess is added. An attempt to obtain a crystalline acid by hydrolyzing the above syrup was unsuccessful, as was also an effort to purify it by means of the barium salt. The compound has well-marked acidic properties and liberates carbon dioxide from aqueous alkali carbonates. No substance corresponding to camphoroxalic acid could be isolated, and, in view of the investigations of Claisen alone,<sup>1</sup> and in conjunction with Hare,<sup>2</sup> and

<sup>1</sup> Ber. d. chem. Ges., 24, 130.

<sup>2</sup> *Ibid.*, 24, 120.

also that of Ruhemann and Hemmy,<sup>1</sup> it appears probable that the above compound is a condensation-product of ethylic oxalacetate resembling some of those described by these workers.

We desire also to record the results of some preliminary experiments which we have made on the condensation of ethylic oxalate and thymol, in presence of sodium. The resulting compound has hitherto only been obtained as an oil. It gives a dark-red coloration with ferric chloride and alcohol, but is apparently not very stable towards alkalis. We have obtained, in addition, some evidence of the simultaneous formation of a substance analogous to camphoroxalic acid. Should further investigation confirm these results proof would be afforded of the reaction of thymol in its "secondary" or tautomeric

form,  $(\text{CH}_3)_2\text{CH}.\text{C} \begin{array}{l} \nearrow \text{CO}.\text{CH}_2 \\ \searrow \text{CH}.\text{CH} \end{array} \text{C}.\text{CH}_3$ , and an interesting field of research amongst other phenols would be opened up.

#### EXPERIMENTAL.

##### *Preparation of Camphoroxalic Acid.*

The method for the preparation of camphoroxalic acid, described in the previous papers on this subject, has been considerably simplified. The product obtained by the action of sodium on camphor and ethylic oxalate (8 or 12 portions) is well shaken with water, the light petroleum solution removed, dried, and the solvent distilled off. The aqueous extract is acidified with dilute sulphuric acid and extracted four times with ether. This ethereal solution is dried, the ether removed, and the residue combined with that from the light petroleum extract. The semi-solid mass is mixed with about 2 liters of water, together with a considerable excess of solid sodium hydrate, and boiled during half an hour; the product is cooled, filtered, and the solid residue repeatedly boiled in the same manner with sodium hydrate solution until a portion of the clear liquid, after acidifying with hydrochloric acid, fails to give a coloration with ferric chloride solution and alcohol. As a rule, about six extractions are required to remove

<sup>1</sup> J. Chem. Soc., 71, 334 (1897).

all the camphoroxalic acid. The combined alkaline liquors are acidified with dilute sulphuric acid and allowed to remain for a short time; the greater portion of the camphoroxalic acid is obtained in crystals, and the remainder by extracting the filtrate once with ether.

*Action of Aniline on Camphoroxalic Acid.*

(1) *Preparation of Phenylcamphoformeneamine.*—Camphoroxalic acid (13.2 grams) is mixed with an equimolecular proportion of aniline (6 grams) and heated in a paraffin-bath at  $130^{\circ}$  for thirty minutes. The reaction proceeds quietly and water is evolved in considerable quantity. The product readily crystallizes on the addition of a solvent, and the yield of crude substance is 10.7 grams. The amine easily dissolves in alcohol, benzene, and ethylic acetate, but only sparingly in light petroleum; it crystallizes in colorless rhombic plates, and occasionally forms very characteristic hair-like needles exceeding an inch in length. Difficulty was experienced in the analysis, due probably to traces of gummy matter which appear to be formed during each recrystallization. For the analysis given below, the specimen was recrystallized six times from ethylic acetate and light petroleum, and benzene and light petroleum, then finally from alcohol, when it melted at  $166^{\circ}$ . The results of the analyses are given below:

I. 0.2800 gram substance gave 0.2112 gram  $H_2O$ , and 0.8158 gram  $CO_2$ .

II. 0.2679 gram substance gave 13.6 cc. nitrogen at  $25^{\circ}.5$  and 743 mm.

	Calculated for	Found.	
	$C_8H_{14} \begin{cases} C : CH \\   \quad   \\ CO \quad NH.C_6H_5 \end{cases}$	I.	II.
C	80.00	79.46	...
H	8.23	8.38	...
N	5.49	....	5.51

The compound gives no coloration, in alcoholic solution, with aqueous ferric chloride. When treated with bromine, in benzene solution, decolorization takes place, hydrogen bromide is evolved, and a precipitate is formed. This substance is colorless, and is probably a hydrobromide; it melts at about

216° and previously darkens. With auric chloride and hydrochloric acid, in alcoholic solution, phenylcamphoformeneamine yields a crystalline compound which is unstable and speedily decomposes, a black amorphous deposit being formed which appears to contain metallic gold. Platinic chloride, under similar conditions, gives a platinochloride,  $(C_{17}H_{21}NO)_2 \cdot H_4PtCl_6$ , which crystallizes in dark, orange-colored needles, and is readily soluble in alcohol, but insoluble in water. The base is not affected by sodium hydrate; when boiled for two hours with a large excess of concentrated aqueous soda it is not perceptibly changed. Proof of the constitution of phenylcamphoformeneamine is furnished by its production from the carboxylic acid, when this is heated above its melting-point either alone or in presence of ethylaniline.

(2) *Preparation of Aniline Phenylcamphoformeneaminocarboxylate*.—Camphoroxalic acid (1 mol.) and aniline (2 mols.) are separately dissolved in the smallest requisite quantity of warm benzene, the solutions mixed and gently heated on the water-bath. The mixture almost solidifies in the course of a few minutes. It is allowed to cool and the mother-liquor drained off. The compound crystallizes from benzene, on the addition of light petroleum, in very small colorless needles melting at 158° with decomposition.

I. 0.2161 gram substance gave 0.1428 gram  $H_2O$ , and 0.5798 gram  $CO_2$ .

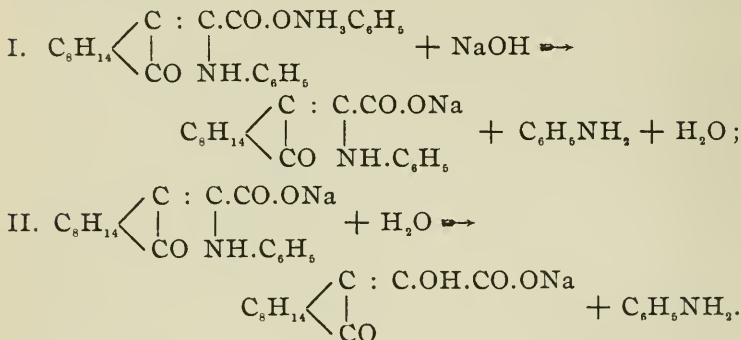
II. 0.1776 gram substance gave 11.7 cc. nitrogen at 19° and 755 mm.

	Calculated for $C : C.CO.ONH_3.C_6H_5$ $C_6H_5 \begin{cases} \swarrow \\ CO \\ \searrow \end{cases} NH.C_6H_5$	Found.	
		I.	II.
C	73.46	73.17	....
H	7.14	7.34	....
N	7.14	....	7.50

The compound is highly unstable in presence of even traces of acid vapors (cf. following reaction), but in an atmosphere free from these it may be retained without decomposition. It is slowly hydrolyzed by water, or even dilute alcohol. With aqueous soda or alcoholic potash decomposition is rapid and takes place in two stages: Aniline and the alkali salt of



phenylcamphoformeneaminecarboxylic acid are first formed, and the latter then slowly decomposes under the continued action of the heated alkali into aniline, and the alkali salt of camphoroxalic acid :



The camphoroxalic acid is recognized by the ferric chloride test, the aniline by the isonitril reaction :

When slowly heated alone, below its melting-point, the compound yields aniline, and phenylcamphoformeneaminecarboxylic acid, which at higher temperatures is resolved into carbonic anhydride and phenylcamphoformeneamine.

*Preparation of Phenylcamphoformeneaminecarboxylic Acid.*—Aniline phenylcamphoformeneaminecarboxylate is triturated with dilute (1 : 6) sulphuric acid, or dilute hydrochloric acid at the ordinary temperature. The salt, without dissolving, immediately acquires a bright-yellow color. The excess of acid, which contains aniline sulphate or hydrochloride, is removed, the residue washed once or twice with cold water, dried, and recrystallized from benzene with the addition of light petroleum. It is readily soluble in the former, almost insoluble in the latter, and is deposited in bright-yellow needles, which resemble iodoform in color, and melt and decompose at 174° when quickly heated. The yield is quantitative.

The compound is also formed by the action of aniline on sodium camphoroxalate. Camphoroxalic acid (2.2 grams = 1 mol.) is dissolved in the smallest quantity of alcohol, water and sodium hydrogen carbonate are added until the solution is clear and has a faintly alkaline reaction. It is now mixed



with aniline (1 gram = 1 mol.), together with more alcohol, if necessary, and the clear liquid allowed to remain during twenty-four hours at the ordinary temperature, and then boiled during fourteen hours in a reflux apparatus. The product is poured into excess of dilute sulphuric acid, extracted with ether, the ethereal solution dried, the ether removed, and the residue purified in the manner described above. The yield is good. Apart from the analyses, the identity of the compounds obtained by both methods of preparation was established by simultaneous melting-point determinations, and also by the fact that a mixture of both in equal proportion melted at the same temperature as either separately.

I. 0.2690 gram substance gave 0.1760 gram  $H_2O$ , and 0.7080 gram  $CO_2$ .

II. 0.2131 gram substance gave 0.1430 gram  $H_2O$ , and 0.5603 gram  $CO_2$ .

III. 0.1882 gram substance gave 8.4 cc. nitrogen at  $29^\circ$  and 742 mm.

IV. 0.1500 gram substance gave 6.6 cc. nitrogen at  $29^\circ$  and 737 mm.

	Calculated for $C_8H_{14}\left\{ \begin{array}{l} C : C.COOH \\ CO NH.C_6H_5 \end{array} \right.$	Found.			
		I.	II.	III.	IV.
C	72.24	71.78	71.70	....	....
H	7.02	7.26	7.45	....	....
N	4.68	....	....	4.74	4.65

Analysis I. was made with a preparation from aniline phenylcamphoformeneaminecarboxylate; for the remainder specimens obtained from sodium camphoroxalate were employed.

Phenylcamphoformeneaminecarboxylic acid readily dissolves in a solution of sodium carbonate, carbonic anhydride being liberated, and also in aqueous sodium hydrate, the solutions being almost colorless. Prolonged boiling with a considerable excess of concentrated aqueous sodium hydrate, in presence of a little alcohol, causes a slow decomposition; aniline is evolved, and camphoroxalic acid is produced, but no

oxalic acid. When heated above its melting-point, or at  $140^{\circ}$  in presence of ethylaniline, phenylcamphoformeneaminecarboxylic acid yields carbonic anhydride and phenylcamphoformeneamine.

*Action of Benzoyl Chloride on Camphoroxalic Acid.*

The formation of a compound (m. p.  $190^{\circ}$ – $191^{\circ}$ ), by the action of acetic anhydride, or of benzoyl chloride, on camphoroxalic acid, has been previously described by Bishop Tingle.<sup>1</sup> It is most readily obtained by boiling the acid (4.4 grams = 1 mol.) with the chloride (4 grams = 1.5 mols.) during fifteen minutes. The product is poured into a solution of sodium hydrogen carbonate; the black pasty mass which separates is dried on a porous plate and recrystallized several times from a mixture of benzene and light petroleum. The yield is not very large. The substance is deposited in minute colorless needles and is not changed by boiling with a solution of sodium hydrate, nor by heating with hydroxylamine in large excess in presence of alkali; bromine, in warm chloroform solution, is also without action on the compound.

I. 0.2520 gram substance gave 0.1844 gram  $H_2O$ , and 0.6788 gram  $CO_2$ .

II. 0.2504 gram substance gave 0.1810 gram  $H_2O$ , and 0.6750 gram  $CO_2$ .

Calculated for $C_{22}H_{30}O_4$ . Mol. wt. = 358.		Found.	
		I.	II.
C	73.74	73.46	73.51
H	8.37	8.13	8.03

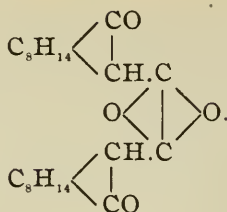
Molecular weight determinations :

Solvent, nitrobenzene.  $r = 7100$ .

Weight of solvent. Grams.	Weight of substance in solution. Gram.	$\Delta$ .	m.
13.7802	0.0605	$0.15^{\circ}$	207.8
13.7802	0.3137	$0.51^{\circ}$	316.9
13.7802	0.7007	$1.09^{\circ}$	331.1

We suggest for this compound the formula

<sup>1</sup> This JOURNAL, 20, 324, 328 (1898).



*Action of Acetic Anhydride on Camphoroxalic Acid.*

Three compounds have been previously obtained<sup>1</sup> by the action of acetic anhydride on camphoroxalic acid. They melted at 118°, 191°, and 242°, respectively, and were all formed in small quantity. The first was shown to be acetylcamphoroxalic acid; the second, also formed by the action of benzoyl chloride on camphoroxalic acid, is described above. We have obtained the third compound in slightly larger quantity, but on account of the poor yield it has not been possible to pursue its investigation to a satisfactory conclusion. It is obtained by boiling camphoroxalic acid (2.2 grams) with acetic anhydride (5.1 grams) during two hours. The product is poured into a solution of sodium hydrogen carbonate. Should it become pasty after remaining in contact with the alkaline liquid for some time, it is removed and dried on a porous plate, otherwise it is extracted by means of ether. It is recrystallized several times from mixtures of benzene or ethylic acetate and light petroleum. In the first two it dissolves very readily but in the last it is practically insoluble. The compound is deposited in small, slender, colorless needles; it gives no coloration with ferric chloride and alcohol; with aqueous sodium hydrate a portion dissolves, and the remainder becomes yellow; bromine, in chloroform solution, is without action on the substance either at the ordinary temperature or when warmed on the water-bath. The yield is only 1.5 grams from 11 grams of acid, and even this is greatly diminished unless the above conditions are adhered to. Resinous bodies only are obtained if the time of heating is from ten to twenty minutes, whilst camphor, which, in varying proportion, always accompanies the crude substance,

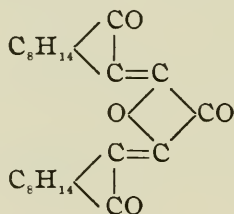
<sup>1</sup> *Loc. cit.*

becomes the chief product when the heating is extended beyond two hours. The purity of the acetic anhydride is also a factor of great importance. At the commencement of the reaction a considerable evolution of carbon dioxide takes place. These observations explain the difficulties previously encountered in connection with the preparation of this compound.

0.2270 gram substance gave 0.1546 gram  $H_2O$ , and 0.6216 gram  $CO_2$ .

	Calculated for $C_{22}H_{28}O_4$ .	Found.
C	75.00	74.68
H	7.60	7.56

A molecular-weight determination by the cryoscopic method failed to give a satisfactory result. It is evident from the foregoing description that the compound originates in consequence of some deep-seated molecular change. Our knowledge of the nature of this and of the reactions of the substance are inadequate for the deduction of its formula with any approach to certainty. We think, however, that the expression



may serve as a first step in this direction, and we believe it to be in harmony with the results of our observations.

#### *Physiological Action of Sodium Camphoroxalate.*

An additional experiment<sup>1</sup> on the physiological action of sodium camphoroxalate has been made with the following results: The dog employed weighed 12.023 kilos and had been used for another experiment which had produced no effect on his circulation. A 2 per cent solution of the sodium camphoroxalate in normal saline solution was introduced into the jugular vein.

<sup>1</sup> We are indebted for it to Prof. Carter of the University of Texas.

Time. P. M.	Blood pressure in mm. mercury.	Pulse in ten seconds.	Dose. cc.	Remarks.
12.50	128	15		
12.50.25			5	
12.50.50	132		5	
12.51.10	132		5	
12.51.20	133		5	
12.52.00	132	15		Struggling respiration throughout entire experiment prevented satisfactory counting of the pulse.
12.53.00	131			
12.54.00	133			
12.54.20			10	
12.55.10	132		10	
12.56.00	140	17	20	
12.56.30	140			
12.56.50	140	22	20	
12.57.00	142			
12.58.00	142	19		
12.58.15			20	
12.59.00	130	17	5	
12.59.40	142			
1.00.00	118			
1.02.30	110	15		
1.02.40			10	These doses were made up from a preparation of sodium camphoroxalate different from that employed in the earlier part of the experiment.
1.03.00	106	15		
1.03.10			10	
1.03.35	120		10	
1.04.00	118	18		
1.04.40	110	17	10	
1.05.00	110			
1.08.00				Killed by chloroform.

These results show that sodium camphoroxalate, even to the extent of 0.241 gram per kilo of body weight, has practically no physiological effect. Death in the former experiments<sup>1</sup> was not due to this, but arose from the escape into the jugular of the solution of magnesium sulphate which was employed to fill the cannula.

#### *Etherification of Camphoroxalic Acid.*

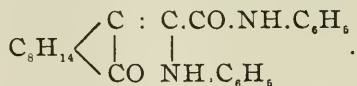
Two experiments were made in the manner previously de-

<sup>1</sup> This JOURNAL, 20, 342 (1898).

scribed<sup>1</sup> to determine the influence of the duration of heating on the yield of ethylic camphoroxalate. The acid (44.8 grams) was dissolved in absolute alcohol (240 cc.) containing 5.91 per cent hydrogen chloride. In the first experiment the solution was boiled during seven and three-fourths hours, in the second one during thirteen hours. The yields were 34 grams and 36.5 grams of ethylic salt, respectively. Absolute alcohol is not always readily attainable, and an attempt was made to modify the conditions so as to permit the employment of ordinary alcohol without unduly diminishing the yield of ester. The acid (45 grams) was dissolved in 90 per cent alcohol (300 cc.), concentrated sulphuric acid (20 cc.) added, and boiled in a reflux apparatus during eleven and a half hours. About one-third of the alcohol was distilled off and the residue warmed on the water-bath with sodium hydrogen carbonate until it was almost neutral and the greater portion of the remaining alcohol had volatilized; it was then poured into water, the neutralization completed with sodium hydrogen carbonate, and the ester extracted with ether. The weight of ester obtained was 42 grams, whilst 2.5 grams of camphoroxalic acid was recovered. The yield of ester, per cent of acid employed, was, in the three experiments, 75.9, 81.5, and 93.3, respectively.

*Action of Aniline on Ethylic Camphoroxalate.*

No reaction appears to take place when aniline and ethylic camphoroxalate, in equimolecular proportion, are boiled in a reflux apparatus with ether or benzene. A mixture of the ethylic salt with two molecular proportions of aniline, when heated at 130° during three hours, gives a good yield of phenylcamphoformeneaminecarboxylic anilide,



The compound readily crystallizes, and is purified by repeated solution in benzene and precipitation with light petroleum; it is finally deposited in small colorless needles melting at 193°.

<sup>1</sup> This JOURNAL, 20, 331 (1898).



Bromine, in chloroform solution, appears to be without action on the anilide, only a very slight diminution of the color is perceptible, and no evolution of hydrogen bromide can be detected. The compound is very stable towards alkalies, no change taking place by heating it on the water-bath, in dilute alcoholic solution, with recently precipitated lead hydroxide, during six hours, nor with sodium hydroxide during thirty minutes; prolonged boiling of the soda solution gives a similar negative result. Attempts to hydrolyze the anilide by the action of sulphuric acid have not, as yet, led to definite results; the products are usually very resinous.

I. 0.2000 gram substance gave 0.1270 gram  $H_2O$ , and 0.5618 gram  $CO_2$ .

II. 0.1927 gram substance gave 0.5420 gram  $CO_2$ .

III. 0.3058 gram substance gave 20.6 cc. nitrogen at  $23^\circ.5$  and 747 mm.

IV. 0.1945 gram substance gave 13.6 cc. nitrogen at  $28^\circ$  and 744 mm.

V. 0.1673 gram substance gave 12 cc. nitrogen at  $26^\circ.5$  and 743 mm.

	Calculated for $C_{24}H_{26}N_2O_2$ .	I.	II.	Found. III.	IV.	V.
C	77.00	79.60	76.70	....	....	....
H	6.95	7.05	....	....	....	....
N	7.49	....	....	7.44	7.50	7.75

Some difficulty was encountered in determining the carbon, hence, in order to avoid, if possible, the formation of graphite, analysis II. was carried out in a current of moist oxygen.

An unsuccessful attempt was made to prepare the aurochloride and platinochloride by mixing an alcoholic solution of anilidocamphoformeneaminecarboxylic anilide, containing a little hydrochloric acid, with alcoholic solutions of auric chloride and platinic chloride, respectively, and allowing the liquid to evaporate spontaneously. The gold salt was reduced and the solution deposited a dark resinous mass; from the platinum solution reddish crystals were obtained, but after purification they became colorless, melted at about  $190^\circ$ , and consisted of the original anilide. If formed at all, the platinochloride is evidently unstable.

*Oxidation of Ethylic Camphoroxalate Phenylhydrazide.*

Ethylic camphoroxalate phenylhydrazide was suspended in absolute alcohol and mixed with recently precipitated pasty anhydrous mercuric oxide, but no action took place after remaining at the ordinary temperature during ten days. Anhydrous ether was substituted for the alcohol, and the mixture boiled during seventeen hours. As only a slight darkening was perceptible, the ether was removed and benzene added, but no effect was produced by ten hours' additional boiling at the higher temperature so obtained. The oxidation takes place readily by the action of hydrogen peroxide in ethereal solution. Aqueous hydrogen peroxide (10 vols. per cent U. S. P.) is extracted three times with ether; the combined extracts, which equal the aqueous solution in volume, are dried, and added to the phenylhydrazide ground to a paste with ether. The hydrazide quickly dissolves, and the solution is allowed to remain over night at the ordinary temperature. After removing the ether a red crystalline residue is obtained which is recrystallized from benzene. From this solvent apparently two kinds of crystals are deposited, hexagonal plates, and tufts of needles. Fractional recrystallization from ethylic acetate, with the addition of light petroleum, gives, by spontaneous evaporation, red needles, which, when crushed, form a white powder and melt at  $210^{\circ}$ .

0.2973 gram substance gave 22.7 cc. nitrogen at  $23^{\circ}.5$  at 746 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \left\{ \begin{array}{l} \text{C} : \text{C.CO.O.C}_6\text{H}_5 \\ \text{CO} \text{ N} : \text{N.C}_6\text{H}_5 \end{array} \right.$	Found.
N	8.23	8.42

The compound is only slowly attacked by glacial acetic acid, in which respect it differs from the original hydrazide.

The less soluble fraction of the oxidation-product, after further purification, melted at  $108^{\circ}$ – $109^{\circ}$ . It was obtained only in very small quantity, and could not be completely freed from traces of hydrazide. It is probably identical with the compound (m. p.  $112^{\circ}$ ) described by Bishop Tingle in a previous paper.<sup>1</sup>

<sup>1</sup> *Loc. cit.*

*Action of Isoamylic Alcohol on Camphoroxalic Acid.*

Camphoroxalic acid (44.8 grams) was dissolved in isoamylic alcohol (240 cc.) containing hydrogen chloride (10.99 grams = 4.57 per cent), and boiled during nine hours. The greater portion of the alcohol was then distilled off, and the residue washed with sodium hydrogen carbonate solution, which removed 3.7 grams camphoroxalic acid. The product could not be induced to crystallize. Since it evidently contained isoamylic alcohol it was heated during a considerable time on the water-bath, at first in an open vessel and finally in a current of dry air under reduced pressure. It failed to give crystals by this treatment, so a portion was distilled under a pressure of 25 mm.; some alcohol passed over, but above 95° decomposition commenced, and the same result took place when another portion was distilled in steam. When hydrolyzed, camphoroxalic acid was quantitatively regenerated from the crude substance.

*Preparation of Ethylic Pyrotartrate.*

Pyrotartaric acid (25 grams) was dissolved in absolute alcohol (100 cc.) containing hydrogen chloride (3.38 grams), and the solution boiled during four and a half hours. The alcohol was distilled off on the water-bath, the residue dissolved in ether, and washed with a solution of sodium hydrogen carbonate. The ethereal solution was then dried and the ether removed. The yield of ester was about 80 per cent of the theoretical. Sulphuric acid may be substituted for the hydrogen chloride with equally good results.

*Action of Ethylic Pyrotartrate on Camphor.*

For the reasons detailed in the theoretical portion of this paper we commenced a study of the interaction of ethylic pyrotartrate and camphor in presence of sodium and of sodium ethoxide. Ethylic pyrotartrate (28.7 grams) and camphor (34.5 grams) were dissolved in light petroleum (250 cc.), and sodium wire (3.5 grams) added. A slow action took place, but heating on the water-bath during three hours was required to bring it to completion. The product, after standing

over night, was poured into water and the petroleum removed, giving solution *A*. The aqueous liquid was extracted with ether, giving solution *B*. It was then acidified with dilute sulphuric acid and again extracted several times with ether, giving solution *C*. After removal of the solvents the residues *A* and *B* were united and warmed with aqueous potash. Apart from borneol and camphor, the only definite product that could be obtained was pyrotartaric acid. Solution *C* yielded an oily residue, which gave a red coloration with alcohol and ferric chloride, showing that a condensation-product of ethylic pyrotartrate and camphor had been produced. The compound is comparatively unstable towards alkali, since, when heated with dilute sodium hydrate, it is converted into its constituents. In a second experiment the mixture of ethylic pyrotartrate, camphor, sodium wire, and light petroleum, in the same proportions as before, were boiled during ten minutes, and then absolute alcohol (10 cc.) was added through the reflux apparatus. The subsequent treatment was similar to that described above, and gave essentially the same result, as did also an experiment in which a dilute, absolute alcoholic solution of sodium ethoxide was employed in place of the sodium wire and light petroleum. The investigation will be resumed at the first opportunity.

*Action of Ethylic Oxalacetate on Camphor.*

Ethylic oxalacetate (18.8 grams) and camphor (22.8 grams) were dissolved in light petroleum (250 cc.), and sodium wire (2.3 grams) added. A reaction readily took place, and was completed by gently warming on the water-bath. The product was treated in the manner described above in the first experiment with camphor and ethylic pyrotartrate. On acidifying the aqueous solution, after the removal of the borneol, etc., the liquid acquired a blue-purple color, which disappeared on agitation with ether, the latter becoming yellow. The residue from the ethereal solution was oily, and an attempt was made to hydrolyze it by warming it with aqueous alcoholic potash. This produced a dark-red solution. The heating was continued until a drop of the alkaline liquid com-

pletely dissolved in a large volume of water. It was then acidified and extracted with ether. After removal of the ether, the residue was again oily, and could not be induced to crystallize. The compound has well-defined acidic properties and liberates carbonic anhydride from a solution of sodium carbonate. With hydrochloric acid in slight excess the blue color is produced as described above, but it disappears on the addition of a larger proportion of acid. When the compound is heated under reduced pressure (50 mm.) an evolution of gas commences below  $95^{\circ}$ . The barium salt is colorless and sparingly soluble, but attempts to purify the acid by means of it did not lead to definite results. The borneol extract, formed during the preparation of the above compound, was examined for an acid corresponding to camphor-oxalic acid, but without success. The probable nature of the compound is discussed in the theoretical portion of this paper.

*Action of Ethylic Oxalate on Thymol.*

Ethylic oxalate reacts with thymol in solution in light petroleum, in presence of sodium wire. The product has hitherto been obtained only as an oil and appears to be somewhat unstable. It gives a dark-red coloration with alcohol and ferric chloride. We have also obtained some evidence of the production of a compound corresponding to camphor-oxalic acid, but have not hitherto succeeded in isolating it from the admixed borneol and camphor. We are continuing this research in various directions.

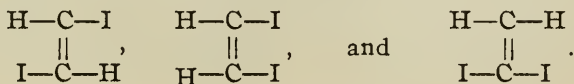
LEWIS INSTITUTE, CHICAGO, ILL.

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## ON A LIQUID ACETYLENE DIIODIDE.

BY EDWARD H. KEISER.

According to our present theories of the constitution of organic compounds two symmetrical and one unsymmetrical acetylene diiodide are possible. The constitution of these is represented by the following formulas :





The first and second represent stereoisomers, the former being the fumaric, the latter the maleic form.

Up to the present time but one acetylene diiodide has been obtained with certainty. This is the well-known solid crystalline compound melting at  $73^{\circ}$  and boiling at  $192^{\circ}$ , which is obtained by conducting a current of acetylene through a solution of iodine in alcohol or in potassium iodide.

A liquid acetylene diiodide is mentioned by Sabanejeff,<sup>1</sup> who prepared the crystalline diiodide from acetylene and an alcoholic solution of iodine, and found that the alcoholic solution from which the solid diiodide had separated gave, on the addition of water, an oily liquid. This liquid, when cooled down, solidified. A few degrees above  $0^{\circ}$  it again partially liquefied. The liquid part was poured off from the solid (the latter was found to be the crystalline diiodide) and again cooled down and solidified. On warming, the portion which first melted was again poured off, and this process of freezing and melting was repeated several times until no more solid diiodide could be removed from the liquid substance. An analysis of this liquid indicated that it had the same percentage composition as the solid acetylene diiodide, and its empirical formula was found to be  $C_2H_2I_2$ .

Sabanejeff apparently obtained but small quantities of this liquid since he was unable to characterize the compound sharply. He states that at a few degrees below  $0^{\circ}$  it becomes solid, its specific gravity is 2.942 at  $21^{\circ}$ , and that it decomposes on distillation.

In 1889 Paterno and Peratoner,<sup>2</sup> in studying the action of acetylene upon iodine in alcoholic and acetic acid solution, were unable to obtain the liquid diiodide of Sabanejeff. The oily liquid which separates on adding water to the alcoholic mother-liquor from which the crystalline diiodide has been removed is not, according to Paterno and Peratoner, a definite compound but a mixture. They also obtain the oil by acting upon a solution of iodine in glacial acetic acid with acetylene. One-fifth of the weight of the oil is solid diiodide, the remainder consists of a liquid, which is found by analysis and molec-

<sup>1</sup> Ann. Chem. (Liebig), 178, 120.

<sup>2</sup> Gaz. Chim. Ital., 19, 1889; and 20, 670.



ular weight determination to have the formula  $C_4H_4I_2O_2$ . They studied the behavior of this liquid compound with phosphorus pentachloride and obtained acetyl chloride. Treated with sodium amalgam, it gave acetic acid; oxidation with chromic acid likewise gave acetic acid. From these facts they conclude that the constitution of the compound is to be represented thus:  $CH_3COO—CI=CHI$ .<sup>1</sup>

*Action of Acetylene upon Iodine.*

In attempting to prepare the solid acetylene diiodide by the direct action of acetylene upon iodine, without the intervention of a solvent, 10 grams of iodine crystals were put into a 500 cc. flask and the air in the flask was displaced by acetylene. The gas was prepared from calcium carbide, and was purified by passing it through a series of wash-bottles containing nitric acid, alkaline lead solution, concentrated caustic potash, and copper sulphate in the order mentioned. The acetylene then was dried with calcium chloride before entering the flask.

Acetylene is apparently without action upon iodine in the cold. On warming the flask so that the iodine melts and the interior is filled with the violet vapor, a slow absorption of the gas begins. Instead of heating the flask with a free flame, as was done in the earlier experiments, it was found preferable to suspend it in a paraffin bath, and to keep the temperature of the bath at from  $140^{\circ}$ – $160^{\circ}$ . Under these conditions a slow but regular absorption of acetylene takes place, and after from twenty-four to thirty-six hours the color of the iodine will have disappeared. When cold, the flask contains a mass of crystals, but also an amber-colored liquid, which can readily be poured off from the crystals. The yield of liquid appeared to be greater if the temperature of the bath was kept at from  $150^{\circ}$ – $160^{\circ}$  than if the temperature was  $120^{\circ}$ – $130^{\circ}$ .

The crystals obtained in this way are the ordinary well-known solid acetylene diiodide. They melt at  $73^{\circ}$ . The liquid that is poured off from the crystals is saturated with the solid diiodide, and on cooling it down to  $0^{\circ}$  a further quantity of the crystals separate. On cooling the liquid to

<sup>1</sup> Beilstein: *Organ. Chemie*, I, 196.

$-23^{\circ}$  it completely solidified. On warming gently and pouring off the portion which first melted, then freezing this part again, partially melting and pouring off the liquid, and repeating this process three or four times, a liquid was obtained which had a constant boiling-point, *viz.*,  $185^{\circ}$ , and which solidified at  $-21^{\circ}$ .

Another method of separating the liquid from the crystalline diiodide depends upon the difference in solubility of the two substances in 50 per cent alcohol. The liquid compound is somewhat soluble in alcohol of this strength; the solid is practically insoluble. If then the liquid compound containing some of the solid diiodide in solution is shaken up with 50 per cent alcohol, the liquid dissolves, and the solid remains behind. On pouring off the alcoholic solution and adding water, the liquid compound is precipitated and separates as a heavy oil.

The pure liquid compound thus obtained is clear and colorless; in diffused daylight it slowly turns violet in color; the same change takes place rapidly in the sunlight. It is insoluble in water, readily soluble in alcohol and organic solvents. It boils at  $185^{\circ}$  (uncorr.) and solidifies at  $-21^{\circ}$ . It is readily volatile with steam. Its specific gravity at  $20^{\circ}$  is 3.0625. It gives no precipitate with ammoniacal cuprous chloride.

The following results were obtained on analysis:

0.2561 gram substance gave 0.0785 gram  $\text{CO}_2$ , and 0.0166 gram  $\text{H}_2\text{O}$ .

0.2389 gram substance gave 0.3931 gram  $\text{AgI}$ , and 0.0030 gram metallic  $\text{Ag}$  (Carius' method).

These results indicate that the formula of the compound is  $\text{C}_2\text{H}_2\text{I}_2$ .

		Calculated.	Found.
$\text{C}_2$	24.0	8.58	8.36
$\text{H}_2$	2.0	0.715	0.72
$\text{I}_2$	253.7	90.705	90.37
	<hr/> 279.7	<hr/> 100.000	

The vapor of this liquid acetylene diiodide can be heated to

230° without decomposition, and a determination of the molecular weight of the compound was made by the vapor-density method of Victor Meyer. Thymol was used as the heating fluid, boiling at 230°.

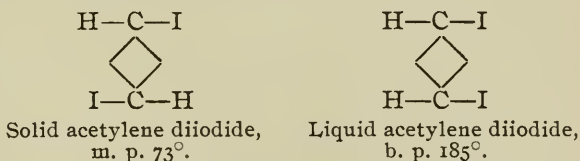
0.0749 gram substance gave 6.2 cc. air at 19° and 753 mm. pressure.  $D = 10.3$ .

	Calculated.	Found.
Molecular weight $C_2H_2I_2$	280	296

An interesting fact noticed in regard to this liquid acetylene diiodide is that when it is allowed to stand in contact with aqueous hydriodic acid it is slowly changed into a mass of crystals. This change takes place more rapidly if the acid is warmed on the water-bath. These crystals melt at 71°, and an examination shows that they are the ordinary solid diiodide.

With zinc dust the alcoholic solution of the liquid diiodide evolves acetylene.

From these facts the conclusion seems justified that this new liquid acetylene diiodide is a stereoisomer of the solid diiodide, and stands in the same relation to the solid diiodide that maleic acid does to fumaric acid. The following space-formulas represent this relationship :



That the liquid diiodide should have the unsymmetrical formula  $H_2C=CI_2$  seems very improbable on account of the behavior of the substance as described above and also on account of its great stability in the air. Aside from the slight color change produced by light it seems to be entirely unaffected by air. The unsymmetrical chloride and bromide,  $CH_2=CCl_2$  and  $CH_2=CBr_2$ , are very unstable substances. They readily undergo polymerization, and they absorb oxygen from the air, forming acetyl derivatives.

## A SIMPLE COLOR REACTION FOR METHYL ALCOHOL.

BY S. P. MULLIKEN AND H. SCUDDER.

In view of the importance of methyl alcohol to the chemist, and its frequent formation in organic reactions, it is surprising that there should be any lack of convenient and simple tests for its identification. Some such tests have been devised for the detection of wood spirit, but they are acetone and not methyl alcohol reactions. At the present time only two direct tests for methyl alcohol are generally recommended by authorities on organic analysis, and of these neither is of such a character as to be extensively and freely used in the every-day practice of the laboratory.

One of these methods, due to Rich and Bardy,<sup>1</sup> depends on the successive conversion of methyl alcohol into methyl iodide, dimethylaniline, and methylaniline violet, by a series of complicated operations that require about twelve hours for their performance. By this method, which, were it not for its tedious length, would have much to commend it to the analyst, one part of methyl alcohol may be detected with certainty in the presence of more than 100 parts of ethyl alcohol.

The second test alluded to, that of J. T. Miller,<sup>2</sup> depends on the oxidation of methyl alcohol to formic acid by means of a mixture of potassium dichromate and sulphuric acid, and the subsequent detection of the formic acid, after distillation, by its reducing action on a hot solution of silver nitrate. This test can be made in about half an hour, and is not seriously interfered with by the presence of relatively large quantities of ethyl alcohol. Its conclusiveness is, however, impaired by the fact that many soluble and volatile compounds besides methyl alcohol, *e. g.*, acetone and allyl alcohol, are also oxidized to formic acid under the prescribed conditions.

The simple test-tube reaction, whose description follows, can be directly applied to the aqueous solution of any organic distillate of low boiling-point, and completed in less than five

<sup>1</sup> Compt. rend., 80, 1076.

<sup>2</sup> Allen's Organic Analysis, 3rd Edition, 1, 81.

minutes. Like all tests of its class, it has limitations that it is important to recognize ; but its results are certainly less liable to misinterpretation than those of the much-used Lieben reaction for ethyl alcohol, which it excels in delicacy.

A piece of rather light copper wire is wound around a lead pencil, so as to form on one end a close spiral about 2 cm. in length. The spiral is then superficially oxidized in the upper flame of a Bunsen burner, and while still at a bright red heat, plunged into 3 cc. of the alcoholic solution contained in a test-tube. This treatment oxidizes a portion of the methyl alcohol to formic aldehyde. A second dip with the oxidized spiral is usually advisable, and in dealing with solutions containing less than 0.1 per cent. of methyl alcohol, as many as three or four additional dips, the tube being cooled each time with tap water. This method of oxidation has the important advantage over others tried, that it does not go too far, and does not give troublesome by-products. *A concentrated spirit should always be diluted with at least three or four volumes of water before oxidation.*

One drop of a 0.5 per cent aqueous solution of resorcin is next added to the weak solution of formic aldehyde, and the mixture very cautiously poured down the side of an inclined test-tube containing a few centimeters of concentrated sulphuric acid. The presence of methyl alcohol is indicated by the appearance of a pure rose-red zone at the line of demarcation between the denser and lighter layers. In and above this very characteristic band of color is suspended a scanty white or pinkish coagulum, which, after long standing, increases notably in color intensity, and finally separates and rises in purplish-red flocks.

In testing for traces of methyl alcohol, the use of a large excess of resorcin is to be carefully avoided. Too much of this reagent tends to destroy the purity of the rose color besides rendering the test less delicate. Thus, while 1 drop of a 0.5 per cent solution of resorcin is the best quantity for use in testing solutions containing 0.1 per cent of methyl alcohol, 0.01 of a per cent of methyl alcohol can be recognized only when the quantity of resorcin is reduced to one-tenth of



that employed in the first instance, and the mixture then allowed to stand for an hour or more.

It is to be remembered that the more common methyl esters and ethers are all slightly hydrolyzed when dissolved in water. Such solutions, since they contain free methyl alcohol, also give this reaction. The only other compounds examined by us, which, when tested in the manner just described, give colorations in the least resembling that caused by methyl alcohol, are secondary and tertiary butyl alcohols, dimethylethylcarbinol, and formic acid. In the case of these rare secondary and tertiary alcohols, the pink zone is separated from the acid by a lower band of lemon-yellow, and the red coloring-matter does not separate and rise to the surface in solid flakes. The coloration from formic acid is so faint as to be scarcely noticeable, even when the solution tested contains as much as 5 per cent of the acid. To preclude the possibility of mistakes arising from the presence of formic acid, mixtures that react strongly acid should be neutralized by the addition of a little sodium carbonate before distillation.

Most primary alcohols are oxidized by the hot copper spiral to aldehydes, and these aldehydes, on treatment with sulphuric acid and resorcin, then yield oxyfluorones or other more or less colored condensation-products of undetermined composition. Fortunately, so far as our experiments enable us to judge, none of the colors produced in this way needs be mistaken for that given by methyl alcohol. Ethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl, octyl, capryl, and allyl alcohols, as also ethyl ether, acetone, furfurol, lactic acid, and the carbohydrates, arabinose, dextrose, lævulose, sucrose, maltose, and lactose, all give shades of yellow, amber or ocherous-brown.<sup>1</sup> The polyatomic alcohols like glycerin and erythrite give brownish-purples. Chloroform and many other non-oxygenated bodies give no coloration whatever. We desire particularly to emphasize the failure of the carbohydrates to give red colorations with sulphuric acid and

<sup>1</sup> The investigations of Mylius and of v. Udranszky (*Zeit. f. physiolog. Chem.*, **11**, 492; **12**, 355 and 377), show that the brownish colorations given by the carbohydrates must be attributed to a reaction between resorcin and furfurol. The latter compound is always present among the products of the decomposition of carbohydrates by sulphuric acid.



resorcin, because certain remarks made during the discussion of this paper, when read before the Chemical Section of the American Association for the Advancement of Science, last August, left the entirely erroneous impression on the minds of many who were present, that the same red coloration would be produced by the carbohydrates under these circumstances, as is shown in the Fischer and Jennings reaction,<sup>1</sup> in which the glucoside condensation-products yielded by carbohydrates and resorcin under the influence of hydrochloric acid are oxidized in alkaline solution by Fehling's reagent.

In dealing with mixtures which contain color-producing organic constituents not removable by neutralization and distillation, it is also a fortunate circumstance that the rose color due to formic aldehyde usually tends to make its appearance in a state of greater or less purity in a narrow band next to the acid, while the other color forms a wider zone just above and shading into the first. When the substances that give the yellow or brown color are present in large excess, the delicacy and certainty of the reaction may be seriously impaired or destroyed. One part of methyl alcohol may, however, be detected without great difficulty in the presence of five, and after a little practice, though with less certainty, in as many as ten parts of ethyl alcohol.

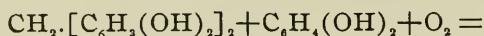
Several color reactions between formic aldehyde and phenols have been recommended at different times for diagnostic purposes, but we find no evidence on record that the colored substances formed in these tests have ever been isolated or identified. Möhlau and Koch have, however, shown<sup>2</sup> that resorcin and formic aldehyde are easily condensed by sulphuric acid to methylenediresorcin; while Caro,<sup>3</sup> from the closely related methylenediphenol and methylenedisalicylic acid, by the use of sulphuric acid and an oxidizing agent, has synthesized the red colors aurin and aurintricarboxylic acid. Now since either phenol or salicylic acid, when substituted for resorcin in the test for formic aldehyde, give rose-colored bands and flakes scarcely distinguishable in hue from those pro-

<sup>1</sup> Ber. d. chem. Ges., **27**, 1350.

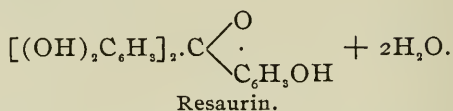
<sup>2</sup> *Ibid.*, **27**, 2887.

<sup>3</sup> *Ibid.*, **25**, 941 and 948.

duced by the use of resorcin, one might naturally suspect that the color from resorcin would be resaurin:



Methylenediresorcin.



Resaurin.

Upon studying the action of solvents on the red flakes, this explanation at first seemed discredited. Resaurin is readily soluble in dilute alkalis or in hot alcohol. But the flakes from a methyl alcohol test may be boiled with alcohol for a long time without losing any appreciable portion of their color, which is only darkened, but not dissolved out when treated with alkalis. On the other hand, if formic aldehyde and resorcin in rather concentrated solutions are mixed in the proper proportions, and poured upon strong sulphuric acid, a body is obtained which shows all the properties and reactions of resaurin,—the same behavior with alkalis, acids, and reducing agents, and the characteristic resaurin absorption spectrum. Our study of this question is not concluded, but the indications are, that if the color observed in the test is not caused by a very little resaurin entangled and protected by a great mass of insoluble, colorless condensation-products, it is at least a body chemically related to resaurin—perhaps a diphenylmethane color.

Hehner<sup>1</sup> seems to have been the first to suggest the detection of formic aldehyde by its zone reactions with phenols and sulphuric acid. For this purpose he particularly recommends the employment of carbolic acid. According to our experience, phenol gives a less intense color than resorcin. Hehner also recommends milk or a solution of casein as a substitute for phenol; but casein is not a suitable reagent for the methyl alcohol tests, because the oxidation-products of ethyl alcohol yield with it the same blue color as formic aldehyde; though singularly enough solutions of pure acetic aldehyde did not give us this result.

<sup>1</sup> Analyst, 21, 20; 20, 155.

Lebbin's reaction,<sup>1</sup> which depends on the appearance of a strong red color when formic aldehyde is boiled with a solution of resorcin and caustic soda, gives satisfactory results when applied to aqueous solutions of pure methyl alcohol that have been treated with a hot oxidized copper spiral; but if even small quantities of ethyl alcohol are present it fails completely.

Trillat's reaction between formic aldehydes and dimethylaniline, gives a strong, pure blue color. A solution containing 1 per cent of methyl alcohol and 10 of ethyl alcohol, still gives a blue of admirable purity, while in the presence of even twice this quantity of ethyl alcohol the result is seldom doubtful. The proper execution of the test requires nearly an hour. This is its chief disadvantage. It is occasionally very serviceable as a confirmatory reaction in the examination of mixtures containing so much ethyl alcohol that the test with resorcin, while pointing to the probable presence of methyl alcohol, is not quite conclusive.<sup>3</sup>

MASS. INSTITUTE OF TECHNOLOGY,  
December 7, 1898.

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## REACTIONS FOR THE DETECTION OF THE NITRO-GROUP.

BY S. P. MULLIKEN AND E. R. BARKER.

There are few radicals of equal importance whose detection in organic compounds by direct qualitative tests is so inadequately provided for as is that of the nitro-group. Vortmann, in his "*Anleitung zur chemischen Analyse organischer Stoffe*," enumerates only three reactions designed for this purpose; *viz.*, reduction to the amido-group, formation of chlorpicrin, which may be recognized by its odor when a nitro-compound is boiled with a solution of bleaching-powder,

<sup>1</sup> Ztschr. anal. Chem., 1897, 518.

<sup>2</sup> Compt. rend., 116, 891.

<sup>3</sup> In the current (December) number of the Bulletin de la Société chimique de Paris and in a preliminary article in the Comptes rendus, 19, 235. Trillat has recently published an interesting method for the detection and estimation of methyl alcohol, which, both on account of its intrinsic importance, and of its bearing on the resorcin test, would have received due attention in the present paper, had the authors known of Trillat's work at the time when their manuscript was prepared for publication.

and the reddish or yellowish colorations produced by boiling solutions of alkaline hydroxides.

According to Vortmann all nitro-compounds give the chlorpicrin reaction. This is evidently a mistake, for with the exception of the nitrophenols aromatic nitro-bodies almost never yield appreciable quantities of chlorpicrin. The color reaction with caustic potash is lacking in precision and is never conclusive. It is therefore nearly always necessary to base the identification of the nitro-group on the results of the reduction test and on physical properties. This procedure would be fairly satisfactory, if the products from such reductions only agreed in presenting some one common property or reaction so striking as to be readily recognized. But instead of meeting with uniformity in the appearance and properties of such reduction-products, we find ourselves confronted by phenomena of the greatest diversity; for an amido-compound may be either a liquid or a solid, colored or colorless, fragrant or odorless; it is often a strong base, but it may exhibit none of the more familiar basic properties and reactions. In short, after the reduction has been properly performed, very skilful and critical interpretation of the experimental data may be demanded to prevent the possibility of deception.

The object of this paper is to call attention to two additional qualitative reactions for the nitro-group, which, while seldom seriously interfered with by the presence of other radicals, possess a distinct advantage over the older tests in the singularly clear-cut and definite character of their visible phenomena.

The first of these tests depends on the fact that all nitro-compounds when dissolved in dilute alcohol containing traces of some neutral salt like calcium chloride are very easily reduced to zinc dust by hydroxylamines. This method for obtaining hydroxylamines was first used nearly simultaneously in 1895 by E. Bamberger<sup>1</sup> and by A. Wohl<sup>2</sup> for the preparation of phenylhydroxylamine. The use of calcium chloride as an accelerating agent is due to Wohl. Three years previous to the work of Bamberger and Wohl, V. Meyer<sup>3</sup> had

<sup>1</sup> Ber. d. chem. Ges., **27**, 1347.

<sup>2</sup> *Ibid*, **27**, 1434.

<sup>3</sup> *Ibid.*, **24**, 3528.

prepared various aliphatic hydroxylamines by reducing fatty nitro-bodies with zinc and hydrochloric acid ; but his method is not applicable in the aromatic series. As a qualitative test this reaction is best applied by dissolving 3 or 4 drops of the nitro-body under examination in 3 cc. of 50 per cent alcohol, adding 5 or 6 drops of a 10 per cent solution of calcium chloride, and then heating until violent boiling begins. Chemical action accompanied by frothing will continue for some time without further application of heat. In dealing with unknown compounds it is advisable to allow the mixture to stand from two to five minutes before filtering, although so much time is seldom absolutely necessary. The presence of a hydroxylamine derivative in the filtrate from the reaction may easily be shown by pouring a few drops of the clear liquid into some strongly ammoniacal solution of silver nitrate in dilute alcohol. The hydroxylamines are all powerful reducing agents and we have never met with any nitro-body, which, when treated in the manner just described, does not yield enough hydroxylamine to give either a silver precipitate or a mirror. A white or light yellow precipitate is without significance.

In the aliphatic series this test has been tried successfully with mononitro-derivatives of methane, ethane, and pentane, and with chlorpicrin ; in the aromatic series with mononitro-derivatives of benzene, toluene, naphthalene, chlorbenzene, brombenzene, anisol, cinnamic acid dibromide, benzoic acid, benzenesulphonic acid, and with *p*-nitrophenylpropionic acid ; with dinitro-compounds of benzene, aniline, and phenol ; and with trinitro-derivatives of benzene, toluene, xylene, phenol, and triphenylmethane. The only important classes of nitrogenous carbon compounds not containing the nitro-radical, which, while unable to reduce ammoniacal silver nitrate solution in the cold, were found to gain the power to do so after the treatment with zinc dust, are nitroso, azo, and azoxy bodies. The reduction-products from bodies of the first class are hydroxylamines or hydrazines, while those from the second and third are hydrazo-compounds.

The principle involved in the second reaction for the nitro-group is borrowed from the well-known Coupier process for



the manufacture of magenta. In this process nitrobenzene, in the presence of a little iron and hydrochloric acid, acts as an oxidizing agent in the conversion of "aniline-red oil" into rosaniline. Lange, in studying the mechanism of Coupier's method,<sup>1</sup> demonstrated that nitrobenzene is not necessary to insure the production of pure rosaniline, but that chlornitrobenzene, nitrotoluene, and certain other substituted derivatives may be used to replace it without causing any change in the chemical composition of the dye-stuff resulting, from which he reasoned that the nitro-compound in all such cases furnishes nothing directly to the structure of the rosaniline molecule, but that it simply provides oxygen for the oxidation of the aniline bases. Nitrosobenzene, methylphenylnitrosamine, azo-, azoamido-, and hydrazobenzene, Bismarck brown and helianthine may be mentioned as examples of bodies found to show this behavior.

After numerous experiments, the following procedure was finally adopted as affording the most convenient means for applying Coupier's principle in the form of a simple qualitative test. Three or four drops of the nitro-compound are boiled for two or three minutes in a test-tube with 2 cc. of "aniline-red oil" (made by mixing equal parts of aniline, *o*-toluidine and *p*-toluidine), 2 cc. of distilled water, 2 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and about 1 gram of iron filings. The liquid reagents should be carefully measured from a small graduate, a large excess of acid entirely preventing the appearance of a color, while too little diminishes its intensity and purity. The red color of the rosaniline is best observed by pouring a few drops of the dark-colored liquid produced in the experiment into a test-tube half-filled with dilute acetic acid. A blank test performed in the same manner, except that the nitro-compound is omitted, gives no color, or at most a pale yellow.

The "aniline-red oil" used as a reagent, if not nearly colorless to begin with, should be made so by distillation. It will then remain in good condition several months, if preserved in a closely-stoppered bottle of dark glass.

<sup>1</sup> Ber. d. chem. Ges., 18, 1918.



The rosaniline reaction has been experimentally verified for all the nitro-compounds included in the list given in connection with the description of the silver reduction test, excepting only nitromethane, nitroethane, and chlorpicrin, which are so volatile as to boil off before oxidation can begin; and the trinitro-compounds, which give dirty reddish or greenish-browns. The color from dinitro-compounds is redder than that given by trinitro-bodies, but it is very far from having the strength or purity of that obtained from substances containing only a single nitro-group.

Upon extending our experiments to compounds not containing the nitro-group, it was soon found possible to lay down the rule, that the appearance of a red color may be generally anticipated whenever an organic body containing oxygen directly linked to nitrogen is subjected to the treatment with aniline bases. Azoxybenzene, nitrosobenzene, methylphenyl-nitrosamine, acetoxime, and ethyl nitrate and nitrite furnish good illustrations of the truth of this statement. Iodobenzene and iodobenzene also give purplish-red solutions, which may perhaps contain fuchsin. Of the two well-known organic oxidizing agents, chloranil and quinone, the first gives only a dirty yellow, and the second a coffee-brown. Other classes of organic compounds, so far as is known, yield no decided colors.

Inorganic oxidizing agents, such as nitrates and nitrites, arsenic acid and mercuric chloride, do not usually give pronounced colorations; but since slight changes in the experimental conditions might lead to the formation of fuchsin, the absence of such substances should be established before giving full weight to the conclusions drawn from any experiment.

After what has been already stated, no detailed comparison of the merits of the three chief tests for the nitro-group will be necessary. As generic reactions, the two new tests, if employed together, will be found to be more uniformly reliable and convenient in practice than the older method of reduction with tin and hydrochloric acid; while on the contrary, the acid reduction process may evidently be made to supply more new and useful data when the problem in hand is to complete

the identification of some particular nitro-compound. None of these methods can furnish absolute proof of the presence of the nitro-radical; but the maximum of certainty attainable by their use alone is reached by the simultaneous employment of the fuchsin with one of the reduction tests—a combination which when a positive result is obtained eliminates the possibility of mistakes that might occur in consequence of the reduction of azo-groupings.

MASS. INSTITUTE TECHNOLOGY,  
December 24, 1898.

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### REVIEWS.

KURZE ANLEITUNG ZUR QUALITATIVEN ANALYSE (EINLEITUNG IN DIE CHEMISCHE ANALYSE; ERSTES HEFT). VON DR. LUDWIG MEDICUS. 8te u. 9te Auflage. Tübingen. H. Laupp. 1898. viii + 158 pp.

Intended as an introduction to the study of chemical analysis in its technical applications, this little book gives, without any preliminary instruction in manipulation, an orderly account of the reactions usually employed for the detection of the more common basic and acid radicals in inorganic compounds, then a rather condensed scheme for the separation of these, an exceedingly brief notice of the rarer elements, with indications of their behavior with the principal group reagents, and at the end a few individual examples for practice. The work is evidently adapted for use, as a kind of syllabus, in laboratory teaching of beginners, and has scarcely anything to distinguish it from the multitude of such little manuals in sundry languages. J. W. M.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW, AND GREASE, FOR LUBRICATION, ETC. By an Expert Oil Refiner. London: Scott, Greenwood & Co. New York: D. VanNostrand Co. Cloth, 8vo. pp. 96. Price, \$3.50 net.

The scope of the book is indicated in the title. In addition a few of the rough-and-ready physical and chemical tests for some of the oils are included. It contains about 60 recipes for mixing all the various oils, from the burning fluids to the heavy cylinder lubricants. In the latter the percentage of animal or vegetable oil recommended is much more than it is customary to employ in this country.

The requirements for the various lubricants, the importance of suiting the oil to the work, the necessity of cleanliness and the general unreliability of oil dealers' data show a thorough familiarity with the subject. The viscosity of the oils is stated in comparison with water, rather than in seconds, as is customary. The use of Gray's flash tester is also unusual.

It is pleasing to note the statement that "the best all-round mineral oils come from America," and that the Russian oils are inclined to clog the machinery. The book would seem to be of great value both to the manufacturer and to the analyst; the price, however, considering its size and value, is disproportionate, if not extortionate.

A. H. GILL.

**LIGHTING BY ACETYLENE. GENERATORS, BURNERS, AND ELECTRIC FURNACES.** By WILLIAM E. GIBBS, M.E. Second Edition, Enlarged and Revised. New York: D. Van Nostrand Co. 1898. 160 pp. Price, \$1.50.

Mr. Gibbs's treatment of acetylene, and of carbide furnaces, is very brief; indeed, though this is the second edition of his book, he does not mention the Horry furnace in which all American carbide is now made, but confines his descriptions to older types. His chapter on lamps and burners is better. He gives the requirements of the New York Board of Fire Underwriters, and an incomplete list of United States patents for furnaces and carbides, and a full list of generator patents. He divides generators into three classes: In the first, water is supplied in measured quantity to an excess of carbide in closed vessels; in the second, the carbide is immersed or withdrawn from water; and in the third, measured quantities of carbide are dropped into a large excess of water. The author concurs with foreign authorities in approving the use of the third type as safer and as furnishing a better quality of acetylene. The beautiful work of Lewes on this subject was published since the first edition of this book, and the author gives an abstract of it.

Mr. Gibbs's book is good, as far as it goes, though by no means exhaustive. In fact the whole subject of acetylene is developing with such rapidity,—new processes elbowing out others scarcely a year old, new suggestions, experiments and practical applications pouring in,—that a book representing the actual state of things to-day would have to be rewritten in a few months, and it is to be regretted that Mr. Gibbs in publishing a second edition did not revise it more thoroughly. Still, as the only book on the subject in English, it will be welcome.

E. R.

**PHYSICAL CHEMISTRY FOR BEGINNERS.** By DR. CH. VAN DEVENTER, with an introduction by PROF. J. H. VAN 'T HOFF. Authorized American Edition from the German Edition. Translated by BERTRAM B. BOLTWOOD, PH.D., Instructor in Physical Chemistry in the Sheffield Scientific School of Yale University. First edition, first thousand. New York: John Wiley & Sons; London: Chapman and Hall, Limited. pp. 154. 1899.

The German edition of Van Deventer's book having been

reviewed in this JOURNAL (Vol. 19, 916), it is only necessary to call attention to the appearance of the American edition.

Whatever may be said in reference to translating an advanced work does not apply to an elementary one. While it is generally true that any one who can read an advanced treatise on a subject can read it in the original (if this is French, German, or English) the same does not hold for elementary books. There are many students of chemistry who can read the translation of Van Deventer's work to good purpose, who would be entirely unable to comprehend it in the original.

A comparison of the translation with the original shows that Dr. Boltwood has done his work with care. H. C. J.

COMMERCIAL ORGANIC ANALYSIS. Second Edition, revised and enlarged; Vol. IV: Proteids and Albuminous Principles; Proteoïds or Albuminoïds. By ALFRED H. ALLEN. Philadelphia: P. Blakiston's Son & Co. 1898.

The present volume is something more than a treatise on analytical methods or a handbook for the detection and determination of adulterations. It includes a more or less systematic exposition of the chemistry of the proteids, their derivatives and related products; indeed, few of the larger textbooks on physiological chemistry contain a more comprehensive compilation of the more recent investigations in the domain considered. Some of the papers of the past year even have found mention, being included in part in an addendum at the end of the volume.

The arrangement of the topics has apparently been determined to a large extent by the main plan of the work, *i. e.*, the presentation of the appropriate methods of commercial analysis. Of the subject matter little is to be said in the way of unfavorable criticism. The descriptions of the best methods to be employed in analysis have occasionally not been presented with as great detail as might be desired, but references to the literature are extensively given and thus the original papers readily become available to the reader who demands more precise information.

In view of the rapid advances which the chemistry of the proteids has made in recent years, it is satisfactory to find an analytical handbook which has not failed to record the results of the later investigations. The methods for the detection and distinction of the various proteids as they occur in natural or artificial products are carefully considered; thus the zinc sulphate method of Bömer for the estimation of proteoses has been introduced, and the various methods for determining proteid nitrogen are reviewed, the very satisfactory Gunning-Kjeldahl process being appropriately treated in detail. We



fancy, however, that the distillation apparatus illustrated (p. 32) will scarcely recommend itself to analysts who are accustomed to conduct a large number of determinations with far simpler arrangements. About one-third of the volume is devoted to the chemistry and analysis of milk and milk products, a large number of useful tables and valuable data regarding milk-adulteration legislation being introduced. The extensive experience of the author renders the treatment of this subject as well as the succeeding chapter on meat and meat-products of particular interest. Allen's method for the separation of the meat bases from proteids by means of bromine—to which Dr. H. W. Wiley has recently called attention (Bulletin No. 54, U. S. Dept. Agr., 1898)—is presented at length (p. 320). The method, if confirmed by a wider experience, promises to solve some of the more difficult problems connected with the analysis of meat extracts and proteid-decomposition products. The composition and preparation of the more prominent commercial proteid food-products, which are being introduced in such large numbers at present, is briefly given.

To avoid the confusion which the older significance of the term "albuminoid" might occasion, the author has found it desirable to introduce the word "proteoïd" for the class of substances (*e. g.*; gelatin, keratin, chitin, etc.) closely resembling the proteids proper. This step is only to be commended; on the other hand, the attempt at a structural formula to represent the constitution of albumin (p. 375)—a structure based upon an obviously incorrect empirical formula of a compound of unknown constitution—seems rather absurd in a book of this character. The compound lysatine, referred to in several places (pp. 16, 370, 385), has recently been shown to be a mixture of lysin and arginin; the albumose described by Sal-kowski as being present in the white of egg (p. 41) has become the ovomucoid of later writers. Lastly, not all physiological chemists will be inclined to admit that elastin (here classed with the fibroïds) contains no sulphur (p. 505).

There has long been a demand for a comprehensive and progressive handbook of the type which Mr. Allen has presented in Vol. IV of his "Commercial Organic Analysis." It covers a field which very few other books have treated equally well—a fact which assures the volume an appreciable acceptance.

LAFAYETTE B. MENDEL.

COMMERCIAL ORGANIC ANALYSIS, a Treatise on the Properties, Proximate Analytical Examination and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, etc., with Concise Methods for the Detection and Determination of Impurities, Adulterations and Products of Decomposition, etc. By ALFRED ALLEN, F.I.C., F.C.S., Public Analyst for the West Riding of Yorkshire and the City of Sheffield; Past President Society of Public Analysts of England, etc. Third edition, illustrated, with revisions and addenda by the author and HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Metallurgy in the Pennsylvania College of Dental Surgery and in the Wagner Free Institute of Science. Vol. II. Part I. pp. 382. Fixed Oils, Fats, Waxes, Glycerol, Nitroglycerin, and Nitroglycerin Explosives. Philadelphia: P. Blakiston's Son & Co. 1899. 382 pp. Price \$3.50.

"Allen's Organic Analysis" being so widely and favorably known, it seems to the writer that the review of a new edition can be best effected by stating the changes which have been made.

It being thirteen years since the appearance of the second edition, it was necessary to rewrite the whole book, an addition of sixty-four pages having been made to the matter treated; this in many cases consists of a description of the methods of the American Association of Official Agricultural Chemists.

The later methods of oil analysis are carefully and critically discussed, as for example, Twitchell's method for the detection of rosin, the bromine thermal method, and the use of the Amagat and Jean refractometer. A useful table is given for the reduction to the standard of the specific gravity of oils taken at a different temperature.

The value of the book would have been increased were the saponification *values* as well as the *equivalents* given, the latter term not having found general acceptance. While the discussion of the technology and properties of linseed oil is very exhaustive, that of lard oil is short and incomplete, which the American user will regret. In this connection it should be borne in mind that in several cases, as would be expected, adulterants of the oils are given, which never occur in this country. A serviceable addition would seem to have been a table of the approximate relative prices of the various oils and the outline of a method for examining an unknown oil.

The chapters upon soaps, explosives, and recovered oils are admirable and contain much new material, the admiralty tests being given; in the case of the oils we note the omission of the Ordway apparatus for the determination of their liability to spontaneous combustion, an account of which was published about eight years ago. Some of the illustrations seem unnecessary, as for example, the apparatus for determining the melting-points of fats, while those of the various refractometers, the use of which is described, are omitted.

A. H. GILL.



# AMERICAN CHEMICAL JOURNAL

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## ON THE HYDROLYSIS OF ACID AMIDES.

BY IRA REMSEN.

Investigations<sup>1</sup> carried out many years ago in this laboratory by myself and a number of younger co-workers showed conclusively that generally speaking an oxidizable group like methyl, ethyl, etc., situated in the ortho position relatively to an unoxidizable group or atom ( $\text{NO}_2$ , Br,  $\text{SO}_2\text{OH}$ ,  $\text{SO}_2\text{NH}_2$ ) in an aromatic hydrocarbon is protected to a remarkable degree from oxidation when the oxidizing agent is chromic acid, whereas a similar oxidizable group situated in the meta or the para position is easily converted into carboxyl by the same oxidizing agent. This protective influence is shown very clearly in the two following cases: (1, 3, 4)-Metaxylenesul-

phonamide,  $\text{C}_6\text{H}_3$   $\left\{ \begin{array}{l} \text{CH}_3 \quad (1) \\ \text{CH}_3 \quad (3) \\ \text{SO}_2\text{NH}_2 \quad (4) \end{array} \right.$ , yields the monobasic acid of

the structure  $\text{C}_6\text{H}_3$   $\left\{ \begin{array}{l} \text{COOH} \quad (1) \\ \text{CH}_3 \quad (3) \\ \text{SO}_2\text{NH}_2 \quad (4) \end{array} \right.$ ; and the sulphonamide of

the structure  $\text{C}_6\text{H}_3$   $\left\{ \begin{array}{l} \text{CH}_3 \quad (1) \\ \text{CH}_3 \quad (4) \\ \text{SO}_2\text{NH}_2 \quad (5) \end{array} \right.$ , derived from paraxylene,

yields the monobasic acid  $\text{C}_6\text{H}_3$   $\left\{ \begin{array}{l} \text{COOH} \quad (1) \\ \text{CH}_3 \quad (4) \\ \text{SO}_2\text{NH}_2 \quad (5) \end{array} \right.$ . It is true that

<sup>1</sup>This JOURNAL, 1, 32, 114; 2, 50, 130, 405, 413; 3, 204, 426; 4, 142, 197; 5, 106, 149.

to a slight extent the other methyl group in both cases is attacked, but there is no doubt of the fact that it is almost completely protected under the conditions named.

One exception to this rule was observed. When the sul-

phonamide of mesitylene,  $C_6H_2 \left\{ \begin{array}{l} CH_3 \quad (1) \\ SO_2NH_2 \quad (2) \\ CH_3 \quad (3) \\ CH_3 \quad (5) \end{array} \right.$ , is treated with

chromic acid, it is converted into the monobasic acid of the

formula,  $C_6H_2 \left\{ \begin{array}{l} COOH \quad (1) \\ SO_2NH_2 \quad (2) \\ CH_3 \quad (3) \\ CH_3 \quad (5) \end{array} \right.$ , which appears as the correspond-

ing sulphinide,  $C_6H_2 \left\{ \begin{array}{l} CO \\ SO_2 > NH \\ CH_3 \\ CH_3 \end{array} \right.$ .

Later some experiments were made with the object of learning whether reducible groups, more particularly the nitro-group ( $NO_2$ ), situated in the ortho position to groups or atoms that are not changed by reducing agents, are also protected. Great difficulties were encountered in the course of this work, and the results have not yet been published. These experiments have recently again been taken up but, although some results of value have been obtained, it does not at present appear that it will be profitable to follow this line of work farther.

Much later than the work on oxidation phenomena above referred to came that of Victor Meyer<sup>1</sup> and his students on the esterification of aromatic acids, which shows that when a carboxyl group is situated in the ortho position to two other groups or atoms, as in the dibrombenzoic acid of the formula,

$C_6H_3 \left\{ \begin{array}{l} Br \quad (1) \\ COOH \quad (2) \\ Br \quad (3) \end{array} \right.$ , it is protected from the action of agents

which generally have the power to convert acids into their esters. Meyer did not seem to recognize the close connection between his results and those previously obtained in this laboratory; at all events he does not mention them and the most

<sup>1</sup> Beginning Ber. d. chem. Ges., 27, 510.

favorable view that can be taken of this omission is that he was not familiar with them.

Kellas<sup>1</sup> at the suggestion of Meyer studied the rate of esterification of monosubstituted benzoic acids, and of saponification of the esters of such acids, and in an elaborate article which appeared in 1897 gave an account of the interesting results reached by him. In general, he found that substituted benzoic acids containing the substituting atom or group in the ortho position are converted into their esters much more slowly than the corresponding meta or para acids; and, conversely, that the esters of such ortho acids are saponified much more slowly than the corresponding meta or para compounds.

In 1889 Remsen and Burton<sup>2</sup> found that, while parasulphaminebenzoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{NH} \end{smallmatrix}$ , is not acted upon when boiled with dilute hydrochloric acid, benzoic sulphinide,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} \text{NH}$ , is first converted into the corresponding

ortho acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{NH}_2 \end{smallmatrix}$ , and then into the acid ammo-

nium salt of orthosulphobenzoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{ONH}_4 \end{smallmatrix}$ ,

by dilute hydrochloric acid. This remarkable difference naturally led to a desire to investigate the action of dilute acids upon acid amides in general—not only those derived from sulphonic acids, but also those derived from carbonic acids. The investigation was, however, delayed for want of a satisfactory method of measuring the rate of change. It was comparatively an easy matter to show that, for example, the amides of benzoic acids containing substituting atoms or groups in the ortho position are more slowly converted into ammonium salts than are the corresponding meta or para acids, but it seemed most desirable to find a refined method by which the exact amount of the change could be determined under a variety of conditions. While we were engaged in testing vari-

<sup>1</sup> Ztschr. phys. Chem., 24, 221.

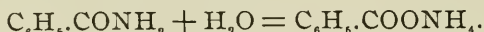
<sup>2</sup> This JOURNAL, 11, 403.

ous methods that suggested themselves, and after we had succeeded in devising one that meets all the requirements of the investigation, J. J. Sudborough, P. G. Jackson, and L. L. Lloyd<sup>1</sup> published an account of their investigation of the rate of hydrolysis of the three brombenzamides. They used concentrated sulphuric acid to effect the hydrolysis and reached the conclusion that orthobrombenzamide is "somewhat more stable than the other two." Before the publication of their article the writer had given<sup>2</sup> a brief account of the first results of this investigation. The work has been continued since that time by Dr. Reid, and his account of it follows.

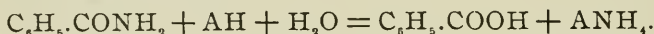
#### EXPERIMENTS ON THE HYDROLYSIS OF ACID AMIDES.

BY E. EMMET REID.

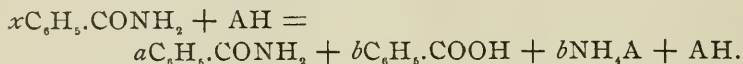
When an acid amide is heated with a dilute acid it is, as is well known, generally transformed into the corresponding ammonium salt, the elements of water being added as, for example, in the case of benzamide:



Of course, in the presence of the acid used to effect the change, the ammonium salt represented in the above equation will be converted into free benzoic acid, so that the equation should be written thus:



This equation represents the result of complete hydrolysis of the amide. But the reaction requires time, and the time is dependent upon the concentration of the solutions, the temperature, and the nature of the amide. During the course of the reaction, at any time before it is complete, the following equation will represent the substances present, leaving out of consideration the effect of dissociation:



If at any stage of the reaction it were possible to determine how much nitrogen is present as ammonium salt, as distinguished from that which is present in the amide, or, better, if both forms could be determined, we should have it in our

<sup>1</sup> J. Chem. Soc., 1897, 229.

<sup>2</sup> This JOURNAL, 19, 319.

power to follow the course of the reaction. Following a suggestion of Professor H. N. Morse of this laboratory, we have found that by means of freshly precipitated magnesium hydroxide the distinction between the ammonium nitrogen and the nitrogen of the amide, can be made with accuracy. Special experiments have shown that, while the ammonium salts are completely decomposed by boiling them with magnesium hydroxide, the amides are not affected by this reagent. Many of the amides are, however, easily decomposed by caustic alkalis so that the amount of amide remaining in solution in any given case after the ammonium salt has been decomposed can often be accurately determined.

The method of work consists in subjecting weighed quantities of the amides to the action of dilute acids or alkalis of known strength at carefully regulated temperatures and for known periods of time. At regular intervals of time measured quantities of the solutions are removed, and the two forms of nitrogen, or of ammonia, determined by the method above referred to.

#### *Calculation of Results.*

If  $A$  represents the original concentration of acid or alkali used, and  $B$  that of the amide, then after a time,  $t$ , these will have become  $A-x$  and  $B-x$ . If the reaction proceeds regularly the velocity at any time should depend on the product of the concentrations at the time.

Then

$$v = \frac{dx}{dt} = (A-x)(B-x)K,$$

in which  $K$  is a constant depending on the nature of the reacting substances, and on the temperature.

On integrating 
$$\frac{dx}{(A-x)(B-x)} = Kdt;$$

it becomes 
$$\frac{1}{A-B} \log. \frac{A-x}{B-x} = Kt + C.$$

Making  $x = 0$ , we have

$$\frac{1}{A-B} \log. \frac{A}{B} = C.$$



Substituting this value for  $C$  in the above we get

$$\frac{1}{A-B} \log. \frac{A-x}{B-x} = Kt + \frac{1}{A-B} \log. \frac{A}{B}.$$

Transforming

$$K = \frac{1}{(A-B)t} \log. \left\{ \frac{A-x}{B-x} \cdot \frac{B}{A} \right\}.$$

If ordinary logarithms are used this must be multiplied by 2.3025.

Then

$$K = \frac{2.3025}{(A-B)t} \log. \left\{ \frac{(A-x)}{(B-x)} \cdot \frac{B}{A} \right\}.$$

This equation has been used by a number of chemists. Since  $C_{\infty} = A-B$ ,  $C_t = A-x$ , while  $C_1 - C_{\infty} = A - (A-B) = B$ ,  $C_1 = A$ , and  $C_t - C_{\infty} = A-x - (A-B) = B-x$ , it is the same as van't Hoff's expression

$$K = \frac{2.3025}{C_{\infty}t} \log. \frac{C_t(C_1 - C_{\infty})}{C_1(C_t - C_{\infty})}.$$

The equation

$$Kt = \frac{1}{A-B} \log. \frac{(A-x)}{(B-x)} \frac{B}{A}$$

may be written  $\log. \frac{(A-x)}{(B-x)} \frac{B}{A} = (A-B)Kt$ , or

$$\frac{B}{A} \cdot \frac{A-x}{B-x} = e^{(A-B)Kt} = [e^{(A-B)K}]^t = m^t.$$

Many chemists in testing the equation

$$\frac{dx}{dt} = (A-x)(B-x)K$$

have for the sake of simplicity put  $A = B$ . In case the reaction is slow this would necessitate making  $A$  and  $B$  very large which might be impossible on account of the slight solubility of one of the substances; or, for some other reason, it might be undesirable. By making  $A$  and  $B$  very small when  $K$  is very small, the velocity might be so slight that the exper-

iments would take long periods of time. There is a worse difficulty for, if  $A-B = C$

then 
$$\frac{dx}{dt} = (A-x)(B-x)K$$

becomes 
$$\frac{dx}{dt} = C(B-x)K + (B-x)^2K.$$

Even when  $C$  is large, towards the end of the reaction the velocity gets very small and difficult to measure; but, if  $C = 0$  the velocity sooner reaches a limit where it cannot be measured. Fair results were obtained with  $A = 28 B$ . When  $\frac{24}{25} B$  had been used up, the velocity had about  $\frac{27}{28} \times \frac{1}{25} = \frac{1}{28}$  (nearly) its original value while with  $A = B$  after 96 per cent had been decomposed the velocity would have been only  $\frac{1}{25} + \frac{1}{25} = \frac{1}{12.5}$ , its original value.

In the experiments described in this article,  $B$  was always made 100 in calculating the value of  $\log. \frac{A-x}{B-x}$ ; since  $x$  was most readily calculated in percentages,  $A$  was expressed in corresponding units. This, of course, does not change the value of the fraction.

In all the tables given in this article

$$K = \frac{2.3025}{(A-B)t} \cdot \log. \left\{ \frac{(A-x)}{(B-x)} \cdot \frac{B}{A} \right\}.$$

#### PREPARATION OF MATERIAL.

For the experiments in Groups I and II, commercial ortho-, meta- and paranitrobenzoic acids were recrystallized until they were pure, and then converted into the corresponding amides. For the other experiments, *o*-nitrobenzoic acid was prepared partly from benzoic acid and partly by oxidizing *o*-nitrotoluene with potassium permanganate. *m*-Nitrobenzoic acid<sup>1</sup> was made by nitrating benzoic acid. *p*-Nitrobenzoic acid was obtained by oxidizing *p*-nitrotoluene. For this purpose it was found best to add 200 grams of *p*-nitrotoluene to 1100 grams concentrated sulphuric acid, 1200 cc. water and 750 grams sodium bichromate, in a five-liter flask provided with a condenser

<sup>1</sup> It was found that even much colored solutions of *m*-nitrobenzoic acid can be decolorized, and made to yield very white acid by adding, while hot, a little potassium permanganate and a few drops of sulphuric acid.

tube. The mixture is kept gently boiling for forty or fifty hours. The residue of *p*-nitrotoluene may be recovered by distilling with steam, but it is not worth the trouble. The *p*-nitrobenzoic acid is filtered off, and well washed. It is then dissolved in soda and this solution treated with charcoal. The acid is precipitated with hydrochloric acid and is pure enough for most uses. From 600 grams *p*-nitrotoluene treated as above 45 grams were recovered and 547 grams of *p*-nitrobenzoic acid obtained. Sodium bichromate is far preferable to the potassium salt.

*o*-Chlorbenzoic acid<sup>1</sup> was made by oxidizing *o*-chlortoluene with potassium permanganate. Some of the *o*-chlortoluene was purchased, and some made by the diazo reaction from *o*-toluidine.<sup>2</sup>

*p*-Chlorbenzoic acid was made by oxidizing commercial *p*-chlortoluene with chromic acid mixture which burnt up the most of it.

*m*-Brombenzoic acid<sup>3</sup> was made by heating benzoic acid, bromine and water in sealed tubes. An attempt was made to free it from benzoic acid by passing steam through a flask containing it.<sup>4</sup> It was finally purified by heating to 200°C. with fuming sulphuric acid and afterwards heating alone in a retort to 280°C.<sup>5</sup> After recrystallizing from hot water it was pure.

*p*-Brombenzoic acid<sup>6</sup> was obtained by oxidizing *p*-bromtoluene with chromic acid mixture. Crude bromtoluene was used. This acid is easily obtained in any quantity.

*o*-Iodobenzoic acid<sup>7</sup> was prepared by oxidizing *o*-iodotoluene with nitric acid diluted with twice its bulk of water. Several weeks' boiling is required, and the yield is poor. The acid was filtered off occasionally and the unchanged *o*-iodotoluene returned, with the nitric acid, to the flask for further heating.

*m*-Iodobenzoic acid<sup>8</sup> was obtained by diazotizing *m*-amido-

<sup>1</sup> Richter : Ber. d. chem. Ges., 4, 463 ; Emmerling : *Ibid.*, 8, 880.

<sup>2</sup> Graebe : Ann. Chem. (Liebig), 276, 56.

<sup>3</sup> Hübner : *Ibid.*, 143, 233.

<sup>4</sup> Angerstein : *Ibid.*, 158, 5.

<sup>5</sup> Hübner : *Ibid.*, 149, 131.

<sup>6</sup> Jackson and Rolfe : This JOURNAL, 9, 84.

<sup>7</sup> Kekulé : Ber. d. chem. Ges., 7, 1007.

<sup>8</sup> *m*-Amidobenzoic acid was diazotized according to the directions given for *o*-amidobenzoic acid by Wachter, Ber. d. chem. Ges., 26, 1744.

benzoic acid, which, in turn, had been made by reducing *m*-nitrobenzoic acid. The *m*-iodobenzoic acid was purified by sublimation.

*p*-Iodobenzoic acid<sup>1</sup> was made by oxidizing *p*-iodotoluene, either with potassium permanganate or nitric acid. The latter seemed preferable though it acts slowly. The *o*- and *p*-iodotoluenes were made according to Gattermann's directions for making iodobenzene, using equivalent quantities of *o*- and *p*-toluidines. The yield of the para is good.

*o*-, *m*-, and *p*-Toluic acids were purchased.

*o*-Methoxybenzoic acid was made by oxidizing with potassium permanganate the methyl ether of *o*-cresol, which was made according to Alleman's directions for making the methyl ether of *p*-cresol.<sup>2</sup>

*Preparation of the Amides*.—All of the above acids were converted into their amides as described below. The yields were in some cases nearly quantitative, in others not so good, but always fair.

The acid was dried and powdered and put into a strong flask, slightly more than the calculated amount of powdered phosphorus pentachloride added, and the flask vigorously shaken. Sometimes slight warming was necessary to start the reaction. When the reaction was nearly over the flask was exhausted as nearly as possible by connecting with a filter-pump. The flask was meanwhile placed in a vessel of water which was brought to boiling and kept there for some time. When the phosphorus oxychloride was about all driven off, the acid chloride was cooled and dissolved in several volumes of ether. This solution was allowed to run with vigorous stirring, into a mixture of crushed ice and concentrated ammonia water.

The amides thus made were recrystallized from hot water, usually twice, and found to be pure.

*o*-, *m*-, and *p*-Amidobenzamides were made by heating for several days solutions of the corresponding nitrobenzamides, with ammonium sulphide. The meta-amide is very soluble. It was recrystallized three times.

*o*-Hydroxybenzamide was made by heating oil of winter-

<sup>1</sup> Beran : *Ibid.*, 18, 137; Hofmann : *Ann. Chem. (Liebig)*, 264, 160; Gattermann : *Praxis*, p. 187.

<sup>2</sup> Dissertation, Johns Hopkins University, 1897, p. 8.

green in sealed tubes with concentrated ammonia water. The yield is good. The amide is very soluble.

*p*-Hydroxybenzamide was made by heating ethyl paroxybenzoate in sealed tubes with concentrated ammonia water. Some phenol is formed and the yield of the amide is poor.

*o*-Ethoxybenzamide was made by heating methyl ethylsalicylate with concentrated ammonia water in a sealed tube at 130° C. The methyl ethylsalicylate was prepared by heating in a sealed tube oil of wintergreen, ethyl iodide, and caustic potash in equivalent quantities.

The amides studied seem, in general, to be considerably more soluble than the corresponding acids. The order of solubility is about that of the acids.

*p*-Chlor- and *p*-nitrobenzamides are difficultly soluble, while the *p*-brom-, and *p*-iodobenzamides are very slightly soluble even in hot water.

The melting-points of these amides were taken with a thermometer said by Bender and Hobein to read 0.7° too low at 0° C., 0.5° too low at 100° C., and correct at 200° C. They were as follows :

Amide.	M. p. observed.	Cor.	Given in literature.
<i>o</i> -Nitro-	172-172.2	176.6	173, 174, 176
<i>m</i> -Nitro-	140-140.2	142.7	140, 142
<i>p</i> -Nitro-	196	201.4	198
<i>o</i> -Chlor-	139.9	142.4	139
<i>p</i> -Chlor-	174-174.2	178.3	170
<i>m</i> -Brom-	152.3	155.3	150
<i>p</i> -Brom-	185.2	189.5	186-190
<i>o</i> -Iodo-	179.4	183.6	183
<i>m</i> -Iodo-	182-182.2 <sup>1</sup>	186.5	....
<i>p</i> -Iodo-	210.6-210.8	217.6	....
<i>o</i> -Hydroxy-	137.4	139.9	138
<i>m</i> -Hydroxy-	167	170.5	167
<i>p</i> -Hydroxy-	....	....	162
<i>o</i> -Amido-	....	....	108
<i>m</i> -Amido-	....	....	75, 78, 79
<i>p</i> -Amido-	178.3-178.6	182.9	178-179
<i>o</i> -Methoxy-	126.5	129.0	128-129
<i>p</i> -Methoxy-	....	....	162-163
<i>o</i> -Ethoxy-	130	132.1	132-135
<i>o</i> -Toluic	139.8	142.8	138
<i>m</i> -Toluic	93	94.0	....
<i>p</i> -Toluic	157.5	160.8	151-159

<sup>1</sup> Sublimed 180°.



The following amides were successfully analyzed for nitrogen by dissolving in 200 cc. water, adding 10 grams caustic soda and distilling off the ammonia into acid, which was 0.1433 normal.

Amide.	Weight.	No. cc. of acid.	N <sub>2</sub> .	Found N per cent.	Calculated N per cent.
<i>m</i> -Nitro- <sup>1</sup>	250 mg.	10.48 cc.	= 21.03 mg.	8.42	8.49
"	" "	10.51 "	= 21.06 "	8.44	8.49
<i>p</i> -Nitro- <sup>1</sup>	250 "	10.50 "	= 21.07 "	8.44	8.49
"	" "	10.63 "	= 21.33 "	8.55	8.49
<i>m</i> -Amido-	232 "	10.62 "	= 21.31 "	9.19	9.15
<i>m</i> -Brom-	226 "	7.89 "	= 15.79 "	6.99	7.05
<i>p</i> -Brom-	301 "	10.47 "	= 21.00 "	6.97	7.05
<i>o</i> -Chlor-	234 "	10.70 "	= 21.47 "	9.18	9.07
<i>p</i> -Chlor-	234 "	10.60 "	= 21.27 "	9.10	9.07
<i>m</i> -Toluic	203 "	10.47 "	= 21.00 "	10.35	10.44
<i>p</i> -Toluic	203 "	10.51 "	= 21.08 "	10.39	10.44

## EXPERIMENTS.—GROUP I.

*Hydrolysis of o-, m- and p-Nitrobenzamides with Hydrochloric and with Sulphuric Acids.*

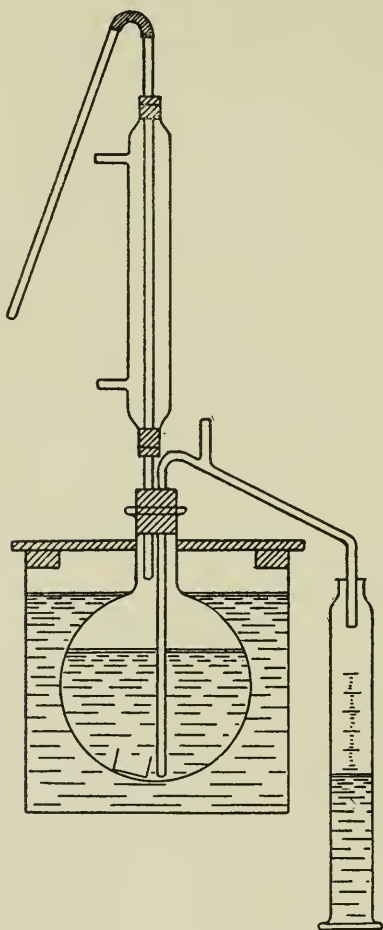
*Apparatus for Heating Amides, and Method of Taking Samples.*

600 cc. of the acid of the desired strength were placed in a 1-litre balloon flask, which was suspended in a covered water-bath containing about 8 litres of water, which was kept vigorously boiling. It was generally kept full by a constant level attachment. Sometimes the water which was run in was heated previously. The water-bath was surrounded by asbestos and the cover was furnished with the same. The flask was provided with a rubber stopper carrying 2 tubes like a wash-bottle except that the one which reached only through the stopper was straight and its upper part surrounded by a Liebig condenser jacket some 30 cm. in length, while the exit tube extended out beyond the edge of the bath and was provided with a T blown on just beyond its highest point.

When it was certain that the acid in the flask had reached the temperature of the bath the stopper was momentarily removed and the amide, which had been weighed out in a light open-mouthed capsule, was dropped in and the flask shaken for one or two minutes so as to insure the complete solution

<sup>1</sup> That is,—in the amide group.

of the amide. The time was kept by a watch which was always set at a chosen hour exactly, so that the samples always fell due when the hands were in the same positions. This makes the timing much easier and prevents many errors.

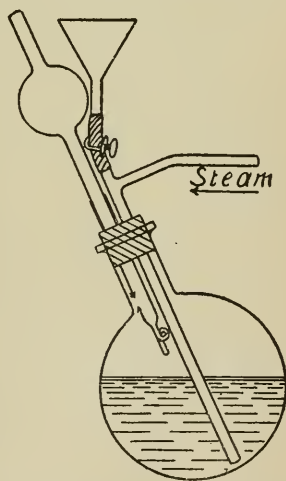


Two flasks were always heated in the same bath. In the one *m*-nitrobenzamide was put, and into the other *p*-nitrobenzamide. The one was put in just five minutes before the other, and exactly the same interval was allowed in taking out the samples.

At the proper time the desired amount of liquid was forced out by blowing into the upright tube, the branch of the exit tube being closed until the moment the liquid ceased flowing, when it was opened so as to allow that portion in the outer part of the tube to flow out. The amount taken out each time was as near as convenient to 75 cc. The sample was received in a 250-cc. cylinder containing 150 cc. cold water. In this way the temperature is immediately reduced to about  $45^{\circ}$  C. at which the reaction would, at best, go on extremely slowly, and the acid is diluted to about one-third of its former strength. The operation of taking a sample required about three seconds. After the taking of each sample the outer part of the exit-tube was washed out by pouring a little alcohol down the branch tube. The samples were poured into flasks, the cylinder being washed out twice each time. These flasks were set aside in regular order, and analyzed in the order in which they were taken out.

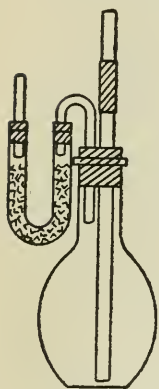
*Analysis of Samples.*—The sample to be analyzed was poured into a balloon containing about 750 cc. and washed out twice, the washings being added to the sample. 10 cc. of a solution containing 0.5 gram of magnesium sulphate to the cubic centimeter was added, and then caustic soda solutions in small portions until a slight precipitate of magnesium hydroxide remained after shaking, and finally 2 to 2.5 cc. of a solution of the same containing 0.26 grams sodium hydroxide per cc., which was known to be enough to precipitate about two-thirds of the magnesium as hydroxide.

The flask was connected by means of a bulb-tube with a block-tin condenser, and the ammonia distilled off in the usual manner. Steam was passed into it meanwhile to expedite the carrying over of all the ammonia. The tube which carried in the steam had a branch at its highest point which was



closed but which was opened when the steam was cut off, to prevent "sucking back." The steam was supplied from a flask containing a little sulphuric acid and potassium bichromate.

The distillate was caught in a 500-cc. Florence flask containing a little more standard acid than was judged sufficient



for the ammonia expected in each case. This flask was closed by a rubber stopper carrying a large tube which extended to the bottom, and at its upper end it was connected to the end of the condenser by a piece of rubber tubing. A smaller tube served to connect the receiver with a U-tube of soda-lime to protect it from the carbon dioxide of the air. When it was thought that sufficient distillate had been collected, the receiver was removed and replaced by a beaker containing litmus. This often showed no trace of ammonia and in most others only minute traces. In some cases an appreciable amount was found, and this was neutralized by a fraction of a

drop of standard acid, which was added to the amount put in the receiver, and the distillation continued until no appreciable amount of ammonia came over.

The burner was turned out and the steam cut off and another receiver containing standard acid was connected with the condenser, and 20 cc. of a solution containing 0.5 gram of sodium hydroxide per cc. was run into the balloon by means of a funnel connected with the branch of the steam tube.

The strong caustic soda solution hydrolyzes the *m*- and *p*-nitrobenzamides in a very short time. In fact, using the above amount it is just as easy to determine the ammonia from these amides as from ammonium chloride. The contents of each receiver were emptied into a beaker, the receiver being washed out with water which had been distilled from acid and then from alkaline potassium permanganate, and kept in a special wash-bottle well protected from the carbon dioxide of the air. The excess of acid was titrated back with standard ammonia, litmus being used as indicator. The method of titration was always the same. The standard am-

monia was allowed to drop in from a burette, stirring meanwhile, until a blue color appeared, a few drops of acid was added, and the ammonia added, a drop at a time, until a blue color appeared, the readings were taken and a few drops of acid added, and then titrated to blue color again, and the readings taken. The results given by these two titrations were averaged each time. A number of test analyses were made by this method which gave satisfactory results.

Each of the amides in question was boiled for hours with the magnesia mixture and no appreciable amount of ammonia could be found in the distillates.

The results were calculated by adding the number of cubic centimeters of standard acid neutralized by the ammonia in the two stages and dividing this into the number neutralized by the first. Hence the strength of the standard acid used was unimportant, yet it was standardized with care.

In the experiments up to Series III cochineal was used as an indicator, and the above precautions to guard against carbon dioxide were not taken, but otherwise the method of analysis was the same.

It was not found practicable to determine *o*-nitrobenzamide as above; hence, in the few experiments made with it, a sample was taken in each of a number of small dry flasks and a measured amount of the solution taken from each; the flasks had been cooled quickly by holding them in a stream of cold water. The amount of decomposition was found by ascertaining the amount of ammonium chloride present by distilling as above with the magnesium hydroxide. In this case the number of cubic centimeters of standard acid neutralized was divided by the number equivalent to the amount of *o*-nitrobenzamide known to have been present in the amount of the solution taken.

In the following tables  $x$  = per cent of decomposition or hydrolysis found.

$t$  = time, always stated in minutes.

$A$  = conc. of acid.

$B$  = conc. of amide, always = 0.04026 N.

## SERIES I.

*o*-Nitrobenzamide with Hydrochloric Acid.

$A = 0.4149$  N.  $B = 0.04026$  N. Titrations with  $H_2SO_4$ ,  
 $0.1419$  N.

4.000 grams put in flask with 600 cc. hydrochloric acid.

No. cc. in sample.	No. cc. of stand. acid neutralized.	Equiv. of total amide in sample in cc. stand. acid.	Per cent. hydrolyzed.	Time in minutes.
96.6	0.95	27.41	3.5	180
91.2	1.03	25.86	4.0	240
82.5	1.33	23.40	6.0	360
86.0	2.16	24.40	8.8	480

The samples taken for times less than three hours were not analyzed as they were then not thought to contain enough ammonia. Corresponding experiments were made with the meta- and para-amides, but the analyses were not all satisfactory, as not enough liquid was caught in the distillations to make sure of the ammonia.

## SERIES II.

*m*- and *p*-Nitrobenzamides.

Conc.  $HCl = A = 0.4896$  N. Conc. amide  $= B = 0.04026$  N. Temp.  $100^\circ$  C. Standard  $H_2SO_4 = 0.1419$  N.

The number of cubic centimeters of standard acid neutralized in the first distillation is given in column 1 and represents the amide hydrolyzed; that neutralized in the second distillation, with caustic soda, represents that not hydrolyzed, or the unchanged part.

*Metanitrobenzamide.*

<i>t</i> .	Changed.	Unchanged.	Total.	Per cent. hydrolyzed.
30	5.35	19.95	25.30	21.1
60	8.70	11.59	20.29	42.8
90	9.69	9.65	19.34	50.1
120	11.39	6.14	17.53	65.0
180	15.12	3.66	18.78	80.5
240	17.88	2.24	20.12	88.9
300	19.69	1.58	21.27	92.6
360	18.81	1.17	19.98	94.2



*Paranitrobenzamide.*

<i>t.</i>	Changed.	Unchanged.	Total.	Per cent. hydrolyzed.
30	5.29	16.41	21.70	24.4
60	8.49	9.11	17.60	48.2
90	12.52	7.22	19.74	63.4
120	13.69	5.55	19.24	71.2
180	16.25	2.97	19.22	84.5
240	19.90	1.75	21.65	91.9
300	24.51	1.41	25.92	94.6
360	19.34	0.63	19.97	96.9

The results for thirty minutes are low, as time is required for solution.

## SERIES III.

Conc. hydrochloric acid =  $A = 0.9792$ .  $B = 0.04026$ .  $A - B = 0.9389$ .  $A/B = 24.35$ . Stand.  
 $H_2SO_4$ , 0.1419 N.

*Metanitrobenzamide.*

$t$ .	Changed.	Unchanged.	Total.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	10.79	14.84	25.63	42.1	2393	57.9	0.0188
60	10.40	4.67	15.07	69.0	2366	31.0	0.0203
90	17.19	3.67	20.86	82.4	2353	17.6	0.0202
120	10.10	1.67	11.77	85.8	2349	14.2	0.0170
150	17.00	1.12	18.12	94.9	2340	5.1	0.0208
180	18.04	0.62	18.66	96.7	2338	3.3	0.0199
210	19.32	0.46	19.78	97.7	2337	2.5	0.0189
240	31.97	0.38	32.35	98.8	2336	1.2	0.0195

Average constant = 0.0194

*Paranitrobenzamide.*

$t$ .	Changed.	Unchanged.	Total.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	10.12	10.29	20.41	49.6	2385	50.4	0.0236
60	15.88	4.90	20.78	76.4	2356	23.6	0.0251
90	17.57	4.37	19.94	78.1	2347	11.9	0.0249
120	20.69	1.28	21.97	94.2	2341	5.8	0.0255
150	16.29	0.68	16.97	96.0	2339	4.0	0.0230
180	20.25	0.30	20.55	98.5	2337	1.5	0.0246
210	21.09	0.28	21.37	98.7	2336	1.3	0.0218
240	46.63	0.45	26.88	99.2	2336	0.8	0.0212

Average constant = 0.0237

## SERIES IV.

HCl conc. =  $A = 0.2448$  N.  $B = 0.04026$ .  $A-B = 0.2045$ .  $A/B = 6.080$ . Standard  $H_2SO_4$ ,  
 =  $0.1419$  N. Feb. 15, 1897.

*Metanitrobenzamide.*

Temp. $100^\circ$ C.	$t$ .	Changed.	Unchanged.	Total.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
	60	4.51	16.33	20.84	21.6	586	78.4	0.0167
	120	9.20	12.57	21.77	42.3	566	57.7	0.0195
	180	11.44	9.06 <sup>1</sup>	21.10	54.2	554	45.8	0.0187
	240	10.94	6.05	16.99	64.4	544	35.6	0.0188
	300	14.42	5.50	19.92	72.4	536	27.6	0.0189
	360	15.24	4.19	19.43	78.5	530	21.5	0.0190
	420	16.87	3.76	20.63	81.8	526	18.2	0.0181
Average constant = 0.0186	480	23.90	3.88	27.78	86.4	522	13.6	0.0188

*Paranitrobenzamide.*

	60	5.78	13.77	19.55	29.5	579	70.5	(0.0246)
	120	10.49	12.28	22.77	46.2	562	53.8	(0.0221)
	180	14.60	8.31	23.91	65.2	543	34.8	(0.0256)
	240	14.84	6.17	21.01	70.6	537	29.4	0.0224
	300	15.35	4.35	19.70	77.9	530	22.1	0.0224
	360	14.21	2.81	17.02	83.5	525	16.5	0.0225
Average constant = 0.0223	420	15.91	2.41	18.32	86.8	521	13.2	0.0220
or 0.0228	480	16.39	1.73	18.12	90.5	518	9.5	0.0223

<sup>1</sup> There is an error here, the cause of which I cannot determine.

## SERIES V.

$\text{H}_2\text{SO}_4 = A = 1.128 \text{ N.}$   $B = 0.04026.$   $A-B = 1.088.$   $A/B = 28.02$  Standard  $\text{H}_2\text{SO}_4 = 0.1419 \text{ N. Feb. 23, 1897.}$

*Metanitrobenzamide.*

Temp. $100^\circ \text{C.}$	$t.$	Changed.	Unchanged.	Total.	Per cent. changed, $x.$	$A-x.$	$B-x.$	$K.$
	30	6.10	13.82	19.92	30.6	2772	69.4	0.01086
	60	9.30	10.28	19.58	46.8	2755	53.2	0.00942
	90	14.48	8.93	23.41	61.9	2740	38.1	0.00963
	120	13.58	4.88	18.38	73.4	2729	26.6	0.00990
	150	15.90	3.94	19.84	80.1	2722	19.9	0.00971
	180	15.05	2.97	18.02	83.5	2719	16.5	0.00904
Average constant = 0.0097	240	17.29	1.56	18.85	91.9	2710	8.1	0.00946
	300	29.21	1.31	30.52	95.8	2706	4.2	0.00961

*Paranitrobenzamide.*

	30	4.45	11.91	16.36	26.9	2775	73.1	0.0093
	60	11.53	10.60	22.13	52.1	2750	47.9	0.0110
	90	11.76	6.03	17.79	66.5	2736	33.5	0.0109
	120	14.79	5.13	19.92	74.9	2727	25.1	0.0104
	150	18.65	3.86	22.51	82.9	2719	17.1	0.0106
	180	19.55	2.81	22.36	87.6	2714	12.4	0.0105
Average constant = 0.0104	240	9.85	0.82	10.67	93.3	2709	6.7	0.0102
	300	22.80	0.88	23.68	96.4	2706	3.6	0.0101

## SERIES VI.

$\text{H}_2\text{SO}_4 = A = 0.564 \text{ N.}$   $B = 0.04026 \text{ N.}$   $A - B = 0.524.$   $A/B = 14.01.$  Standard  $\text{H}_2\text{SO}_4$   
 $= 0.1419 \text{ N.}$  March 1, 1897.

*Metanitrobenzamide.*

Temp. $100^\circ \text{C.}$	$t.$	Changed.	Unchanged.	Total.	Per cent. changed, $x.$	$A - x.$	$B - x.$	$K.$
	60	5.62	14.37	19.99	28.1	1373	71.9	0.00984
	120	9.53	10.06	19.59	48.7	1352	51.3	0.01064
	180	13.26	7.51	20.77	63.8	1337	36.2	0.01140
	240	Flask broke						
	300	14.78	3.69	18.47	80.0	1321	20.0	0.00984
	360	16.46	2.79	19.25	85.5	1316	14.5	0.00989
Average constant = 0.0100	420	14.30	1.96	16.26	87.9	1313	12.1	0.00932
	480	31.48	2.93	34.41	91.5	1310	8.5	0.01046

*Paranitrobenzamide.*

	60	6.11	12.62	18.73	32.6	1368	67.4	0.0117
	120	11.02	9.10	20.12	54.5	1347	45.5	0.0119
	180	14.00	6.26	20.26	69.1	1332	30.9	0.0119
	240	17.80	4.86	22.66	78.6	1322	21.4	0.0118
	300	14.20	2.46	16.66	85.2	1316	14.8	0.0117
	360	16.18	1.89	18.07	89.6	1311	10.4	0.01165
Average constant = 0.0118	420	Sample lost						
	480	19.57	1.01	20.58	95.1	1306	4.9	0.0117

## SERIES VII.

$\text{H}_2\text{SO}_4 = A = 0.2851 \text{ N.}$   $B = 0.04026 \text{ N.}$   $A - B = 0.2448.$   $A/B = 7.07.$  Standard  $\text{H}_2\text{SO}_4$ ,  
 $= 0.1419 \text{ N.}$

*Metanitrobenzamide.*

$t$ .	Changed.	Unchanged.	Total.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
60	2.92	15.79	18.71	15.6	691	84.4	0.00989
120	5.40	13.90	19.30	28.0	679	72.0	0.00975
180	4.47	11.76	19.23	38.8	669	61.2	0.00983
240	9.45	10.60	20.05	47.1	660	52.9	0.00964
300	11.02	9.41	20.43	53.8	653	46.2	0.00942
360	11.20	7.57	18.77	59.7	647	40.3	0.00930
420	12.17	6.63	18.80	64.7	642	35.3	0.00905
480	22.58	9.94	32.52	69.4	638	30.6	0.00919

Temp.  $100.36^\circ \text{ C.}$

Average constant  $= 0.0095$

*Paranitrobenzamide.*

$t$ .	Changed.	Unchanged.	Total.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
60	3.81	18.65	22.46	17.0	690	83.0	0.0109
120	5.44	12.77	18.21	29.9	677	70.1	0.0105
180	8.03	11.62	19.65	40.9	666	59.1	0.0105
240	10.14	10.07	20.21	50.2	657	49.8	0.0106
300	11.19	8.44	19.63	57.0	650	43.0	0.01035
360	11.53	6.57	18.10	63.7	643	36.3	0.0104
420	13.28	5.80	19.08	69.6	637	30.4	0.0105
480	22.40	7.82	30.22	74.1	633	25.9	0.0105

March 10, 1897

Bar. 752.7

Temp.  $99.7^\circ \text{ C.}$

Average constant  $= 0.0105$



## EXPERIMENTS.—GROUP II.

*Hydrolysis of o-, m-, and p-Nitrobenzamides with Alkalies.*

*Heating the Amides.*—The arrangement of the flask in which the hydrolysis was carried on was exactly the same as above described except that the air which was blown into the upright tube was made to pass over soda-lime, and the upright tube was not jacketed with water in the experiments carried on below the boiling temperature. The same water-bath, as above, was used at boiling, but for carrying on the reaction at lower temperatures the flasks were suspended in a large thermostat. This consisted of a tin boiler about 50 cm. by 25 cm. by 40 cm. deep, containing about 40 liters of water. This was heated by a double gas-stove, fed through a large Ostwald gas-regulator of special construction. Much trouble was caused by the frequent breaking of the large glass bulb which contained the solution of calcium chloride until the glass bulb was replaced by a brass tube about 25 mm. in diameter and about 70 cm. in length containing 300 cc. of solution. It was so bent as to extend nearly around the bath several centimeters from the walls and about 7 centimeters from the bottom. A small brass tube some 6 mm. in diameter was brazed into one end. This was bent up vertically and then over the edge of the bath, and was connected with the gas-regulator by means of a firm rubber joint. Instead of providing for a constant supply of gas through the regulator, as is customary, two small "pilot" flames, supplied from an independent source, were placed beside the two stove burners.

The tin boiler was covered with thick asbestos board, and was kept filled to a certain level by being connected through a syphon with a tin vessel containing about 800 cc. of water which was kept within 1° or 2° of the temperature of the bath, by a Bunsen burner controlled by a small Ostwald gas-regulator. This vessel was kept filled by a constant level attachment.

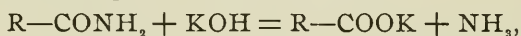
The water in the bath was kept well stirred by a stirrer driven by a water motor. No considerable difference of temperature could be noted in the various parts of the bath.

When the brass tube was filled with an ordinary solution of

calcium chloride, the temperature of the bath when set at 80° or 90° C. was found to sink gradually. This was finally traced to the air originally dissolved in the water from which the solution was made. This air gradually separates out when the bath is kept at a high temperature, and causes the regulator to shut off the gas at too low a temperature. This difficulty was entirely overcome by boiling the solution vigorously and cooling it in a vacuum, and also boiling it in the tube during the filling.

A thermometer, found to read 0.40° C. too high at 100° C. and 0.80° C. too high at 0° C. and having a scale about 40 cm. long extending from 0° to 100° C. on which hundredths could be easily estimated, was kept suspended in the bath and was read from 30 to 70 times during each experiment while the amides were in the bath. At 80°C. or below, the extreme variation could be kept within about 0.1° C., while at 90° C. it was usually about 0.2° C.

*Analysis of Samples.*—Since the reaction



involves the elimination of ammonia which is liable to escape from the alkaline solution, the amount of hydrolysis cannot be determined directly as in the preceding cases. The method adopted was to put the sample in the distilling-flask with magnesium hydroxide and to distil off all ammonia until the distillate came over neutral. Then only, was a receiver with standard acid connected with the condenser and caustic soda run into the distilling-flask to decompose the residual amide and drive over the resulting ammonia. This was titrated in the usual manner. But to determine the per cent of decomposition the total amide must be known. As the same amount of amide was always put into the same amount of solution, this could be readily calculated from the volume of the sample which was found as follows: A 100 cc. measuring-flask was carefully dried and 10.0 cc. of a solution containing 0.5 gram magnesium sulphate per cc. or, when the alkali used was barium hydrate, an equivalent amount of magnesium chloride, measured in from a burette. The sample was blown into this in the usual manner. The caustic alkali of the re-

acting solution is immediately rendered harmless by double decomposition with the magnesium salt. The measuring-flask was then placed in cold water until it had reached the temperature of the room, when it was filled with water from a burette. The capacity of each measuring-flask used was determined by measuring into it the same amount of the magnesium salt solution and filling up to the mark with an alkaline solution of the same strength as that used in the experiments. In this way any error due to the precipitation of the magnesium hydroxide was avoided. To get the volume of each sample it was only necessary to subtract from this figure the amount of water required to fill the flask to the mark  $+10.0$  cc., the amount of the magnesium salt solution which had previously put in. Found in this way the volume of the sample was considered correct to a tenth of a cubic centimeter or to about one part in seven hundred, which was accurate enough, considering other sources of error.

For convenience in calculating results a table was made out, giving for each tenth of a cubic centimeter of the reacting solution, from 65.0 cc. up to 85.0 cc., the volume of standard acid, 0.1433 N., corresponding to the original content of amide.

The caustic potash and caustic soda solutions used, were titrated against standard acid using phenolphthalein and methyl-orange as indicators, in order to determine the amount of carbonate present. This rarely amounted to more than 1 per cent of the whole and was disregarded. The caustic soda was in some cases prepared from the metal in water and in others from a solution of the sulphate and barium hydrate. The following tables give the results. In all cases two flasks the one containing the meta- and the other para-amide, were heated in the same bath.

## SERIES I.

NaOH =  $A = 0.08824$  N.  $B = 0.04026$ .  $A - B = 0.04798$ .  
 =  $0.1419$  N. March 17, 1897.

$A/B = 2.192$ . Standard  $H_2SO_4$ .

*Metanitrobenzamide.*

$l$ .	Unchanged. Sample. cc.	Total cc. acid.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	6.72	68.7	19.59	153.4	34.2	0.499
60	3.24	82.4	23.48	133.1	13.9	0.502
90	1.32	73.2	20.59	125.0	6.4	0.509
120	0.63	81.8	23.31	121.9	2.7	0.523
150	0.27	81.1	23.12	120.8	1.6	0.489
180	0.23	73.3	20.92	120.3	1.1	0.452
210		73.7				
240		19.9				

Temp.  $100.34^\circ$  C.

Average constant =  $0.496$

Were thought to contain too little ammonia for analysis.

*Paranitrobenzamide.*

30	4.62	61.20	17.46	73.1	146.1	26.9	0.629
60	1.34	43.70	12.46	89.2	130.0	10.8	0.590
90	1.04	79.4	22.55	95.3	123.9	4.7	0.576
120	0.51	73.0	20.82	97.5	121.7	2.5	0.538
150	0.28	70.7	20.15	98.6	120.6	1.4	0.509
180	0.15	69.6	19.85	99.2	120.0	0.8	0.489
210		70.8					
240		84.4					

Average constant =  $0.555$

Were thought to contain too little ammonia for analysis.

## SERIES II.

NaOH =  $B = 0.01896$  N.  $A = 0.04026$  N.  $A - B = 0.02130$ .  $A/B = 2.123$ . Standard  
 $H_2SO_4 = 0.1419$  N. March 30, 1897.

*Metanitrobenzamide.*

Temp. of boiling water	$t$ .	Unchanged.	Vol. of sample.	Equiv. of amide in sample.	Equiv. of amide in sample.	Per cent changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
	20	15.30	64.5	8.62	18.30	34.8 <sup>1</sup>	177.5	65.2	0.584
	40	16.10	72.9	9.97	16.10	47.0	165.3	53.0	0.452
	60	15.43	74.0	9.89	21.19	56.2	156.1	43.8	0.405
	80	15.54	79.5	10.62	22.66	66.0	146.3	34.0	0.410
	100	15.30	81.0	10.82	23.09	70.9	141.4	29.1	0.381
	120	13.23	73.0	9.75	20.80	76.7	135.6	23.3	0.395
Average constant =	140	13.64	77.2	10.31	22.00	79.9	132.4	20.1	0.379
0.409	160	9.18	51.7	6.91	14.73	79.5	132.8	20.5	Sample too small

*Paranitrobenzamide.*

	20	15.97	67.0	8.95	19.09	34.0	178.3	66.0	0.565
	40	16.06	76.1	10.17	21.69	54.4	157.9	45.6	0.574
	60	13.50	68.4	9.14	19.49	64.7	147.6	35.3	0.532
	80	14.18	76.1	10.14	21.60	72.9	139.4	27.1	0.507
	100	12.57	71.6	9.57	20.41	80.9	131.4	19.1	0.552
	120	12.53	72.4	9.67	20.63	82.8	129.5	17.2	0.495
Average constant =	140	11.20	65.9	8.80	18.78	85.2	127.1	14.8	0.468
0.531	160	13.02	79.0	10.55	22.51	89.0	123.3	11.0	0.558

<sup>1</sup> In Series II the percentages were calculated from the amount of alkali that became neutralized in the experiment, as the amide was in excess.

## SERIES III.

NaOH =  $A = 0.06497$ .  
0.1433 N. April 27, 1897.

$B = 0.4026$ .  $A-B = 0.02471$ .  $A/B = 1.614$ . Standard HCl =

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Eqiv. of sample.	Percent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	11.96	72.6	20.39	41.4	120.0	58.6	0.321
60	7.35	66.5	18.68	60.7	100.7	39.3	0.312
90	5.00	63.1	17.73	71.8	89.6	28.2	0.304
120	4.82	72.2	20.28	76.2	85.2	23.8	(0.268)
150	2.88	67.3	18.91	84.8	76.6	15.2	0.307
180	2.20	64.2	18.03	87.8	73.6	12.2	0.296
210	1.97	76.1	21.38	90.8	70.6	9.2	0.300
240	1.68	84.0	23.60	92.9	68.5	7.1	0.301

Average constant = 0.305

*Paranitrobenzamide.*

25	10.63	65.7	18.46	42.4	119.0	57.6	0.400
60	5.89	63.2	17.75	66.8	94.6	33.2	0.392
90	4.46	71.9	20.20	77.9	83.5	22.1	0.382
120	3.28	74.0	20.79	84.2	77.2	15.8	0.374
150	2.56	81.6	22.92	88.8	72.6	11.2	0.375
180	1.65	70.4	19.78	91.7	69.7	8.3	0.371
210	1.05	58.9	16.55	93.7	67.7	6.3	0.365
240	0.32	22.2	6.24	94.9	66.5	5.1	0.352

Average constant = 0.376



## SERIES IV.

NaOH =  $A = 0.06734$  N.  $B = 0.04026$  N.  $A-B = 0.02708$ .  $A/B = 1.670$ . Standard  
 HCl =  $0.1433$  N. May 4, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	14.05	67.8	19.04	26.2	140.8	73.8	(0.105)
60	14.35	82.8	23.35	38.3	128.7	61.7	(0.140)
90	9.38	78.7	22.11	57.6	109.4	42.4	0.179
120	6.34	69.2	19.44	67.4	99.6	32.6	0.186
150	5.08	65.1	18.29	72.2	94.8	27.8	0.176
180	4.28	69.5	19.52	78.1	88.9	21.9	0.182
210	3.69	73.0	20.50	82.0	85.0	17.0	0.193
240	3.23	78.6	22.08	85.4	81.6	14.6	0.187

Average constant = 0.184

*Paranitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	12.91	70.3	19.75	34.6	132.4	65.4	0.237
60	9.26	70.0	19.66	52.9	114.1	47.1	0.229
90	5.70	57.7	16.21	64.8	102.2	35.2	0.227
120	4.42	57.0	16.01	72.4	94.6	27.6	0.221
150	3.69	62.9	17.67	79.1	87.9	20.9	0.227
180	3.71	77.8	21.86	83.0	84.0	17.0	0.223
210	2.71	66.3	18.63	85.4	81.6	14.6	0.213
240	2.88	87.8	23.55	87.8	79.2	12.2	0.209

NaOH made from  $\text{Na}_2\text{SO}_4$  and  
 $\text{Ba}(\text{OH})_2$ ,

Average constant = 0.223

## SERIES V.

NaOH =  $A = 0.06923$  N.  $B = 0.04026$  N.  $A-B = 0.02897$ .  $A/B = 1.720$ . Standard HCl = 0.1433 N. May 7, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	18.76	80.8	22.70	17.3	154.7	82.7	(0.097)
60	13.21	67.1	18.85	28.7	143.3	71.3	(0.090)
90	11.94	75.6	21.24	43.8	128.2	56.2	0.108
120	8.87	65.0	18.25	51.4	120.6	48.6	0.106
150	8.66	74.5	20.93	58.5	113.5	41.5	0.109
180	7.27	71.0	19.95	63.6	108.4	36.4	0.105
210	6.12	68.1	19.13	68.0	104.0	32.0	0.105
240	4.33	68.9	19.36	71.9	100.1	28.1	0.107

Average constant = 0.107

*Paranitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	13.55	69.6	19.55	12.8	159.2	87.2	(0.067)
60	11.73	67.5	18.96	28.1	143.9	71.9	(0.087)
90	11.12	72.8	20.45	45.6	126.4	54.4	0.115
120	8.34	61.3	17.22	53.9	118.1	46.1	0.114
150	4.73	42.4	11.91	60.3	111.7	39.7	0.113
180	5.86	62.5	17.56	66.6	105.4	33.4	0.116
210	5.45	61.4	17.25	69.1	102.9	30.9	0.109
240	5.33	74.8	21.02	74.6	97.4	25.4	0.115

NaOH made from  $\text{Na}_2\text{SO}_4$  and  $\text{Ba}(\text{OH})_2$

Average constant = 0.114

## SERIES VI.

NaOH =  $A = 0.06798$  N.  $B = 0.04026$  N.  $A-B = 0.02772$  N.  $A/B = 1.688$ . Standard  
 HCl =  $0.1433$  N. May 17, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Percent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	13.75	54.7	15.39	10.7	158.1	89.3	0.0573
60	16.31	72.9	20.48	20.4	148.4	79.6	0.0597
90	13.86	68.4	19.22	27.9	140.9	72.1	0.0586
120	14.91	80.6	22.64	34.1	134.7	65.9	0.0576
150	11.66	69.2	19.44	40.0	128.8	60.0	0.0579
180	11.85	77.8	21.85	45.8	123.0	54.2	0.0560
210	11.48	81.2	22.81	49.7	119.1	50.3	0.0581
240	10.86	83.8	23.54	53.8	115.0	46.2	0.0584

Average constant =  $0.0584$

*Paranitrobenzamide.*

30	15.61	57.4	16.12	3.4	165.4	96.6	(0.0179)
60	19.69	74.5	20.83	4.0	164.8	96.0	0.0101
90	17.85	66.6	18.71	4.6	164.2	95.4	0.0078
120	18.69	71.6	20.11	7.1	161.7	92.9	0.0092
150	19.47	75.3	21.15	8.4	160.4	91.6	0.0088
180	16.25	76.2	21.41	Distillation not complete			
210	18.26	73.2	20.56	11.2	157.6	88.8	0.0086
250	22.03	90.6	25.45	13.4	155.4	86.6	0.0100

NaOH made from  $\text{Na}_2\text{SO}_4$  and  
 $\text{Ba}(\text{OH})_2$

Average constant =  $0.0091$

## SERIES VII.

$\text{NaOH}' = A = 0.06798 \text{ N.}$   $B = 0.04026 \text{ N.}$   $A - B = 0.02772 \text{ N.}$   $A/B = 1.688.$  Standard  
 $\text{HCl} = 0.1433 \text{ N.}$  May 25, 1897.

*Metanitrobenzamide.*

Temp. 100° C.	<i>t</i>	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A - x</i> .	<i>B - x</i> .	<i>K</i> .
	30	8.42	67.7		55.7	113.1	44.3	0.497
	60	Sample lost						
Average constant = 0.484	90	3.05	73.4	20.62	85.1	83.7	14.9	0.482
	120	1.83	68.5	19.24	90.4	78.4	9.6	0.474

*Paranitrobenzamide.*

	30	7.16	64.9	18.23	60.7	108.1	39.3	0.587
	60	3.69	65.1	18.29	79.8	89.0	20.2	0.576
Average constant = 0.572	90	2.11	63.9	17.95	88.2	80.6	11.8	0.562
	120	1.72	88.3	24.80	93.1	75.7	6.9	0.562

1 Sodium hydroxide made from sodium sulphate and barium hydroxide.—Temperature of boiling water.

## SERIES VIII.

KOH =  $A = 0.06738$  N.  $B = 0.04026$  N.  $A - B = 0.02712$  N.  $A/B = 1.673$ . Standard  
 HCl =  $0.1433$  N. May 28, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	12.04	71.1	19.97	39.7	127.6	60.3	0.289
60	8.02	73.4	20.64	61.1	106.2	38.9	0.301
90	5.20	66.6	18.74	72.3	95.0	27.7	0.295
120	4.13	74.1	20.82	80.2	87.1	19.8	0.297
150	3.28	78.5	22.05	85.1	82.2	14.9	0.293
180	2.36	73.2	20.56	88.5	78.8	11.5	0.289
210	1.94	76.7	21.55	91.0	76.3	9.0	0.285
240	1.52	76.6	21.52	92.5	75.8	7.5	0.276

Average of 79 readings  $90.03^\circ$   
 Max. var.  $0.29^\circ$  C.

Average constant =  $0.291$

*Paranitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	10.65	71.9	20.20	47.3	120.0	52.7	0.379
60	6.56	72.3	20.31	67.7	99.6	32.3	0.376
90	4.58	74.3	20.87	78.1	89.2	21.1	0.380
120	3.20	76.8	21.57	85.2	82.1	14.8	0.368
150	2.54	79.0	22.19	88.6	78.7	11.4	0.348
180	1.77	76.3	21.43	91.7	75.6	8.3	0.347
210	1.12	62.8	17.64	93.7	73.6	6.3	0.341
240	0.78	57.4	16.12	95.2	72.1	4.8	0.337

KOH from  $K_2SO_4$  and  $Ba(OH)_2$

Average constant =  $0.359$

## SERIES IX.

KOH =  $A = 0.06947$  N.  $B = 0.04026$  N.  $A-B = 0.02921$  N.  $A/B = 1.725$ . Standard  
 HCl = 0.1433. June 2, 1897.

*Metanitrobenzamide.*

	$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
80° C.	30	14.33	72.4	20.34	29.5	146.0	70.5	0.209
	60	10.35	70.4	19.78	47.7	124.8	52.3	0.185
Average of 50 readings 79.97° C.	90	7.98	68.8	19.33	58.7	113.8	41.3	0.178
Max. var. = 0.16° C.	120	6.57	71.4	20.06	67.2	105.3	32.8	0.177
	150	5.08	70.8	19.89	74.5	98.0	25.5	0.183
	180	4.46	74.6	20.96	78.7	93.8	21.3	0.178
Average constant = 0.182	210	3.81	74.5	20.93	81.8	90.7	18.2	0.173
	240	2.70	64.1	18.01	85.0	87.5	15.0	0.174

*Paranitrobenzamide.*

	30	12.88	69.7	19.58	34.2	138.3	65.8	0.225
	60	11.17	85.8	24.10	53.7	118.8	46.3	0.226
KOH made from $K_2SO_4$ and Ba(OH) <sub>2</sub>	90	7.02	70.8	19.89	64.7	107.8	35.3	0.217
	120	4.73	61.5	17.28	72.6	99.9	27.4	0.214
	150	4.01	66.5	18.68	78.5	94.0	21.3	0.212
	180	3.65	76.1	21.38	82.9	89.6	17.1	0.211
Average constant = 0.216	210	73.7	73.7	20.71	Sample not analyzed.			
	240	1.91	63.9	17.95	89.4	83.1	10.6	0.214



## SERIES X.

$\text{Ba(OH)}_2 = A = 0.06659 \text{ N.}$   $B = 0.04026 \text{ N.}$   $A - B = 0.02633 \text{ N.}$   $A/B = 1.654.$  Standard  
 $\text{HCl} = 0.1433 \text{ N.}$  June 7, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of Sample.	Equiv. of Sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	11.61	69.9	19.64	40.9	124.5	59.1	0.305
60	7.83	81.9	23.00	66.0	99.4	34.0	0.360
90	4.77	72.0	20.22	76.4	89.0	23.6	0.348
120	3.76	88.5	22.05	83.0	82.4	17.0	0.340
150	2.58	75.8	21.30	87.9	77.5	12.1	0.343
180	1.97	74.3	20.87	90.6	74.8	9.4	0.331
210	1.47	73.9	20.71	92.9	72.5	7.1	0.229
240	0.87	59.4	16.73	94.8	70.6	5.2	0.333

Average constant = 0.336

*Paranitrobenzamide.*

30	10.81	78.3	22.00	50.9	114.5	49.1	0.445
60	5.87	73.3	20.57	71.5	93.9	28.5	0.436
90	4.00	73.1	20.53	80.5	84.9	19.5	0.408
120	2.44	68.7	19.30	87.4	78.0	12.6	0.417
150	2.03	77.8	21.86	90.7	74.7	9.3	0.400
180	1.35	75.8	21.30	93.7	71.7	6.3	0.407
210	0.93	65.7	18.46	95.0	70.4	5.0	0.387
240	0.79	79.3	22.27	96.4	69.0	3.6	0.389

Average constant = 0.409

## SERIES XI.

Ba(OH)<sub>2</sub> =  $A = 0.06772$  N.  $B = 0.04026$  N.  $A-B = 0.02746$ .  $A/B = 1.682$ . Standard  
 HCl =  $0.1433$  N. June 10, 1897.

*Metanitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
80° C.							
30	14.00	73.8	20.73	32.5	135.7	67.5	0.216
60	10.02	72.4	20.34	50.8	117.4	49.2	0.214
90	8.02	74.6	21.05	61.9	106.3	38.1	0.205
120	6.41	77.8	21.86	70.7	97.5	29.3	0.207
150	4.62	68.1	19.13	75.8	92.4	24.2	0.199
180	3.99	72.9	20.48	80.1	88.1	19.9	0.195
210	3.03	67.2	18.88	84.0	84.2	16.0	0.198
240	2.65	71.6	20.11	86.8	81.4	13.2	0.197

Average constant =  $0.204$

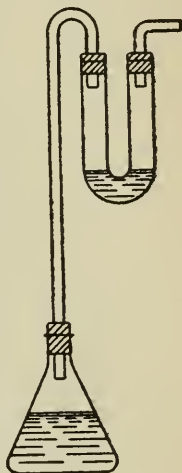
*Paranitrobenzamide.*

$t$ .	Unchanged.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
80° C.							
30	13.03	73.3	20.59	36.7	131.5	63.3	0.257
60	9.15	76.5	21.49	57.4	110.8	42.6	0.264
90	7.09	79.5	22.33	68.2	100.0	31.8	0.253
120	4.66	72.3	20.31	77.1	91.1	22.9	0.261
150	3.76	69.9	19.64	80.9	87.3	19.1	0.242
180	3.06	73.8	20.73	85.2	83.0	14.8	0.243
210	2.10	62.5	17.56	88.0	80.2	12.0	0.239
240	2.04	77.3	21.71	90.6	77.6	9.4	0.241

Average constant =  $0.250$

*Experiments on o-Nitrobenzamide with Caustic Soda at about 100° C.*

It was found impossible to estimate *o*-nitrobenzamide by distilling off the ammonia from it with caustic soda, as was done with the meta- and paranitrobenzamides. This rendered it necessary to retain all the ammonia liberated by the caustic soda during the reaction. To accomplish this the following method was used: 500 mg. of *o*-nitrobenzamide were weighed into a small Erlenmeyer flask and 75 cc. of the caustic soda solution measured in. The flask was closed by a rubber stopper carrying a tube some 30 cm. long, bent over at the top and passing through the stopper of a U-tube containing more than enough acid to neutralize the amount of alkali in the flask. The flask was plunged into boiling water and shaken so as to bring the contents to the required temperature as quickly as possible. At the proper time the flask was removed and shaken in cold water to stop the reaction. By tilting the flask when this was done it could be made to suck back much of the acid in the U-tube. The contents of the flask and the U-tube, together with the washings of both, were placed in a distilling-flask and, after neutralization, the magnesium hydroxide mixture added and the ammonia distilled off in the usual way. The number of cubic centimeters of standard acid neutralized was divided by the volume of standard acid equivalent to 500 mg. of *o*-dinitrobenzamide, to obtain the per cent.



The following table gives the results of a series of four experiments made in this way. The four Erlenmeyer flasks were heated together in the same water-bath, and the temperature considered to be 100° C.

*o*-Nitrobenzamide.

NaOH =  $A = 0.06734$  N.  $B = 0.04026$  N.  $A-B = 0.02708$ .  $A/B = 1.670$ . Standard HCl =  $0.1433$  N. May 4, 1897.

<i>t</i> .	Changed.	Weight of amide. mg.	Equiv. of amide.	Per cent. changed, $x$ .
60	1.98	500	21.07	8.1
125	4.21	"	"	20.0
185	5.34	"	"	25.3
245	6.03	"	"	28.6

## EXPERIMENTS.—GROUP III.

*Hydrolysis of Several Amides with Hydrochloric Acid at the Temperature of Boiling Water.*

*o*-, *m*-, and *p*-Nitrobenzamides; *o*-, *m*-, and *p*-Amidobenzamides; *o*- and *p*-Chlorbenzamides; *m*- and *p*-Brombenzamides; *o*-Iodobenzamide; *o*-, *m*-, and *p*-Toluic amides; *o*-Hydroxybenzamide; *o*-Methoxybenzamide; *o*-Ethoxybenzamide.

*Method of Taking Samples.*—The method of heating the amide with the acid was the same as in Group I. The hydrochloric acid was made up by measuring 100 cc. of c. p. concentrated hydrochloric acid into a two-liter bottle and diluting to a mark near the neck. An acid of about 0.55 N was obtained. From each bottle full, so made up, 600 cc. were measured into each of the three flasks, which were heated at the same time in the same bath. The strength of the acid was found each time by titrating a portion of the remainder with standard caustic potash.

With many of the amides experimented upon, especially those of the ortho series, it was found impossible to determine the undecomposed amide in the samples as was done with the meta- and paranitrobenzamides in the experiments of Group I. Therefore, as in Group II, it was necessary to know the volume of the sample taken. To this end a 200-cc. measuring-flask was taken, rinsed well with water and then with alcohol, warmed, and dried. Into the flask was measured from a burette 4.5 cc. of a solution containing 0.25 gram caustic soda in each cc. A 100-cc. "full" pipette was filled to the mark and also emptied into the flask, into which the sample

was blown as the seconds hand of the watch passed the 60 seconds mark. The force with which the sample was blown in thoroughly mixed it with the water and alkali in the flask. The 4.5 cc. of caustic soda solution used was sufficient to neutralize 50 cc. of the reacting solution. By mixing with the cold water the temperature was immediately brought down to about 50° or 60° C. The flask was put into cold water, where it was allowed to remain ten minutes, being usually shaken several times in that interval, taken out and filled with water from a burette, which, to avoid mistakes, was filled each time to the zero mark. To lessen errors, the water from the pipette and from the burette was allowed to flow with as nearly as possible the same velocity each time. The burette was usually read twice. The measuring flask was emptied into the proper one of a row of 300 cc. Erlenmeyer flasks and washed twice into the same. As 3 flasks containing the reacting mixtures were heated at the same time, this cycle of operations had to be gone through with for each of the 3 flasks every thirty minutes. In the first few series it was not always possible to get ready for a sample at the proper time. In this event the sample was taken several minutes later and the actual time recorded.

Each of the measuring flasks used was calibrated for this special use by drying, measuring in the 4.5 cc. caustic soda solution, and the contents of the 100-cc. pipette, and filling to the mark from the burette.

*Analysis of Samples.*—The sample with 10 cc. of the solution of magnesium sulphate added was emptied into the distilling flask and washed twice into the same. It was nearly neutralized with caustic soda, and finally 2 to 2.5 cc. of a solution of the same, 0.25 gram in 1 cc., added. Instead of taking the trouble and time to neutralize the acid, the amount of the caustic soda solution necessary to neutralize the acid and set free the proper amount of magnesium hydroxide was calculated from the known volume of the sample and that amount added, at once, from a burette.

The ammonia was distilled off with steam, caught in the proper amount of standard acid, and titrated as usual. The amount of standard acid neutralized was divided by the vol-

ume of standard acid equivalent to the amide contained originally in the known volume of the sample taken.

In all titrations cochineal was used as indicator. Some solutions made from the same lot of bugs worked splendidly, while for no known reason others were bad and had to be thrown away. The solution seems to deteriorate after about ten days.

From about the fourth series on, all of the water used for making up the acid, for putting in the measuring flasks, etc., and wherever else it was to go into the distilling flask, was distilled from sulphuric and chromic acids.

The results of the experiments made according to this procedure are given in the following tables. An amount of each amide equivalent to 4.000 grams nitrobenzamide was weighed into each flask, except in several cases where the amide was scarce, and in some experiments with difficultly soluble amides, when half that concentration was used :



## SERIES I.

Conc. of HCl =  $A = 0.5769$  N. Conc. of amide =  $B = 0.04026$  N.  $A - B = 0.5366$ .  $A/B = 14.33$ . Dec. 15, 1897.



$t$ .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	6.25	86.1	24.36	25.6	1407	74.4	0.0172
63½	12.79		27.31	48.6	1384	51.4	0.0178
90	14.38	85.9	24.14	59.6	1473	40.4	0.0179
120	15.66	80.5	22.61	69.3	1364	30.7	0.0176
150	13.92	63.1	17.73	78.5	1355	21.5	0.0184
180	18.10	78.5	22.05	82.1	1351	17.9	0.0172
210	17.13	69.2	17.13	88.1	1345	11.9	0.0183
240	13.39	51.4	14.64	91.5	1342	8.5	0.0171

Average constant = 0.0177

NOTE.—The same concentrations, etc., apply to the tables for  $p$ -amidobenzamide and benzamide. All were heated at the same time.

## SERIES I.—Continued.

*p*-Amidobenzamide, 3.280 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	6.12	81.8	22.97	26.6	1406	73.4	0.0180
66 $\frac{1}{4}$	10.18	72.0	20.22	50.3	1383	49.7	0.0187
94	12.67	71.1	19.97	63.4	1370	36.6	0.0190
120	15.47	75.3	21.16	73.0	1360	27.0	0.0195
150 $\frac{1}{2}$	15.88	69.0	19.38	81.8	1351	18.2	0.0204
180	16.80	67.0	19.07	88.6	1344	11.4	0.0218
210	18.15	70.51	19.81	91.6	1341	8.4	0.0214

Titrations bad

*Benzamide*, 2.917 grams.

40	8.41	82.0	23.03	36.5	1397	63.5	0.0200
69	13.40	86.4	24.27	55.2	1378	44.8	0.0206
93	14.97	80.9	22.72	65.9	1367	34.1	0.0211
122	12.72		17.16	74.1	1359	25.9	0.0210
151	18.68	80.4	22.58	82.7	1350	17.3	0.0209
180	19.44	78.0	21.91	88.7	1344	11.3	0.0219
211	13.06		14.14	92.4	1341	8.6	0.0211

Average constant = 0.0209

## SERIES II.

HCl =  $A = 0.5538$  N.  $B = 0.04026$  N.  $A-B = 0.5135$ .  $A/B = 13.75$ . Standard HCl =  $0.1433$  N. Dec. 17, 1897.

*m*-Brombenzamide, 4.816 grams.

$t$ .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	4.81	73.6	20.65	23.3	1352	76.7	0.0161
60	8.70	68.4	19.22	44.2	1331	55.8	0.0179
90	10.88	64.2	18.03	60.3	1315	39.7	0.0190
120	14.38	72.1	20.25	71.0	1304	29.0	0.0192
150	16.72	74.6	20.96	79.8	1295	20.2	0.0200
180	19.31	80.9	22.72	85.0	1290	15.0	0.0199
210	18.89	75.4	21.18	89.2	1286	10.8	0.0179
240	Volume of sample lost.						

Average constant = 0.0184

NOTE.—Great difficulty was experienced in getting the amides in solution. The insolubility of the acids formed seemed to cause irregularities.

## SERIES II.—Continued.

*p*-Brombenzamide, 4.816 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	3.38	58.2	16.35	20.7	1354	79.3	0.0140
60	6.45	56.0	15.73	41.0	1334	59.0	0.0161
90	10.52	69.9	19.67	53.6	1321	46.4	0.0157
120	13.69	77.3	21.71	63.1	1312	36.9	0.0154
150	12.30	63.2	17.75	69.3	1306	30.7	0.0147
180	13.36	63.9	17.95	74.4	1301	25.6	0.0141
210	14.32	65.3	18.35	78.0	1297	22.0	0.0135
240	15.36	67.2	18.88	81.3	1294	18.7	0.0131

Average constant = 0.0146

*p*-Chlorbenzamide, 3.744 grams.

30	5.22	74.4	20.90	25.0	1350	75.0	0.0170
60	8.11	64.6	18.15	44.7	1330	55.3	0.0181
90	10.43	63.0	17.70	58.9	1316	41.1	0.0183
120	14.57	75.3	21.16	68.6	1308	31.4	0.0180
150	14.90	70.2	19.72	75.5	1300	24.5	0.0175
180	Results lost.						
210	18.22	73.9	20.74	87.8	1287	12.2	0.0189
240	14.16	56.7	15.93	88.8	1286	11.2	0.0172

Average constant = 0.0179

## SERIES III.

HCl =  $A = 0.5451$  N.  $B = 0.04026$  N.  $A-B = 0.5048$ .  $A/B = 13.54$ . Bar. 757.4 cor.  
 Hence b. p. of water =  $99.9^\circ$  C. Standard HCl =  $0.1433$ .

*o-Toluic Amide, 3.256 grams.*

$t$ .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
30	0.76	73.7	20.71	3.7	1350	96.3	0.00229
60	1.50	74.8	21.02	7.1	1347	92.9	0.00226
90	2.57	90.4	25.39	10.1	1344	89.9	0.00218
120	2.56	66.6	18.71	13.7	1340	86.3	0.00211
150	3.30	73.7	20.71	15.9	1338	84.1	0.00213
180	3.83	70.4	19.78	19.4	1335	80.6	0.00222
210	3.73	58.9	16.79	22.2	1332	77.8	0.00221
240	4.87	69.3	19.47	25.0	1329	75.0	0.00222
Average constant = 0.00220							

NOTE.—Amount of ammonia found in first sample about 1.8 mg. *o*-Amides seem to run little ahead at first or else the analyses are too high, but there is so little ammonia that it is hard to decide this point.

## SERIES III.—Continued.

*m*-Toluic Amide, 3.256 grams.

<i>t</i> .	Changed.	Vol. of sample.	Eqiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	4.38	65.0	17.26	25.4	1329	74.6	0.0181
60	8.76	70.1	19.69	44.5	1310	55.5	0.0183
90	11.81	70.3	19.75	59.8	1294	40.2	0.0191
120	13.89	70.1	13.89	70.5	1284	29.5	0.0193
150	14.98	67.8	19.04	78.7	1275	21.3	0.0196
180	15.74	66.6	18.71	84.1	1270	15.9	0.0195
210	17.17	68.5	19.24	89.2	1265	10.8	0.0204
240	23.03	89.4	25.11	91.7	1262	8.3	0.0200

Average constant = 0.0193

*p*-Toluic Amide, 3.256 grams.

<i>t</i> .	Changed.	Vol. of sample.	Eqiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	4.81	71.8	20.17	23.8	1330	76.2	(0.0168)
60	9.13	76.3	21.43	42.6	1311	57.4	0.0173
90	9.32	59.4	16.74	55.7	1298	44.3	0.0170
120	12.88	68.4	19.22	67.0	1287	33.0	0.0175
150	15.93	76.2	21.41	74.4	1280	25.6	0.0172
180	13.46	58.4	16.41	82.0	1272	18.0	0.0182
210	15.68	64.5	18.12	86.5	1268	13.5	0.0176
240	22.78	88.8(?)	24.95(?)	91.3(?)	1263	8.7	(0.0196)

Average constant = 0.0175



## SERIES IV.

HCl =  $A = 0.5538$  N.  $B = 0.4026$  N.  $A - B = 0.5135$  N.  $A/B = 13.75$ . Standard HCl = 10.433 N. January 4, 1898.

*o*-Nitrobenzamide, 4.000 grams.

$t$ .	Changed.	Vol. of sample.	Equiv. of sample, $x$ .	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	0.22	66.8	18.77	1.2	1374	98.8	(0.00073)
60	0.42	68.6	19.27	2.2	1373	97.8	(0.00067)
90	0.45	65.1	18.29	2.5	1372	97.5	0.00050
120	0.70	69.5	19.52	3.6	1371	96.4	0.00055
150	0.99	74.3	20.87	4.7	1370	95.3	0.00058
180	1.00	72.3	20.31	4.9	1370	95.1	0.00050
210	1.16	67.0	18.82	6.2	1369	93.8	0.00055
240	1.66	91.8	25.78	6.5	1369	93.5	0.00051

Average constant = 0.00054

NOTE.—The fact that the amount of ammonia found was so very small may account for the irregularity in the first two 0.22 cc. (= 0.53 mg.  $\text{NH}_3$ ). In this series and those following ammonia-free water was used.

## SERIES IV.—Continued.

*o*-Amidobenzamide, 3.280 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	0.59	59.4	16.68	3.5	1372	96.5	(0.00217)
60	1.20	68.9	19.33	6.2	1369	93.8	0.00194
90	1.47	61.4	17.25	8.6	1366	91.4	0.00180
120	1.77	60.0	16.85	10.5	1364	89.5	0.00167
150	2.46	65.3	18.35	13.4	1362	86.6	0.00174
180	3.15	69.1	19.41	16.2	1359	83.8	0.00178
210	3.53	67.7	19.02	18.6	1356	81.4	0.00178
240	4.97	86.1	24.19	20.5	1354	79.5	0.00174

Average constant = 0.00178

*o*-Hydroxybenzamide, 3.328 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	1.41	62.5	17.59	8.0	1367	92.0	(0.00503)
60	2.63	60.8	17.08	13.7	1361	86.3	0.00445
90	3.76	66.9	18.80	20.0	1355	80.0	0.00451
120	4.91	73.4	20.62	23.8	1351	76.2	0.00413
150	6.18	70.2	19.72	31.4	1344	68.6	0.00460
180	7.73	79.4	22.30	34.8	1340	65.2	0.00435
210	7.18	66.0	18.54	38.8	1336	61.2	0.00429
240	11.49	95.4	26.80	42.9	1332	57.1	0.00429

Average constant = 0.00437

## SERIES V.

HCl =  $A = 0.5520$  N.  $B = 0.04026$  N.  $A-B = 0.5117$  N.  $A/B = 13.71$ . Bar. 757.2 mm.  
 B. P. water  $99.9^{\circ}$  C. Standard HCl =  $0.1433$  N. January 6, 1898.

*o*-Iodobenzamide, 5.944 grams.

$t$ .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A-x$ .	$B-x$ .	$K$ .
60	0.80	67.5	18.96	4.2	1367	95.8	(0.00130)
120	1.34	67.5	18.96	7.1	1364	92.9	(0.00119)
150	1.65	70.8	19.96	8.2	1363	91.8	0.00104
180	2.03	71.5	20.08	10.1	1361	89.9	0.00108
210	2.27	70.7	19.84	11.5	1359	88.5	0.00105
240	2.58	67.6	19.00	13.6	1357	86.4	0.00111
270	3.00	73.6	20.68	14.5	1056	85.5	0.00105
300	3.54	79.1	22.22	16.0	1355	84.0	0.00106

Average constant = 0.00106

NOTE.—Here again the first or the first and second samples run ahead, but it may be only apparent, as the amount of ammonia is very small.

## SERIES V.—Continued.

*o*-Chlorbenzamide, 3.744 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
60	1.69	62.6	17.59	9.6	1361	90.4	0.00395
120	4.12	73.3	20.59	20.0	1351	80.0	0.00339
150	4.00	61.5	17.28	23.1	1348	76.9	0.00320
180	4.95	65.9	18.51	26.8	1344	73.2	0.00317
210	5.52	64.7	18.17	30.3	1340	69.7	0.00315
240	6.31	64.7	18.17	34.7	1336	65.3	0.00326
270	7.55	70.5	19.81	38.1	1333	61.9	0.00327
300	11.19	97.4	27.36	40.9	1330	59.1	0.00322

Average constant = 0.00321

*o*-Hydroxybenzamide, 3.328 grams.

60	2.71	68.4	19.22	14.1	1357	85.9	(0.00463)
120	4.97	68.4	19.22	25.9	1345	74.1	(0.00458)
150	6.17	73.2	20.56	30.0	1341	70.0	0.00432
180	7.95	81.6	22.92	34.7	1336	65.3	0.00436
210	7.59	69.5	19.52	38.9	1332	61.1	0.00433
240	9.39	77.3	21.71	43.3	1328	56.6	0.00439
270	8.90	66.9	18.80	47.3	1324	52.7	0.00440
300	11.59	81.0	22.75	50.9	1320	49.1	0.00440

Average constant = 0.00437

## SERIES VI.

HC1 =  $A = 0.557$  N.  $B = 0.04026$  N.  $A-B = 0.5154$ .  $A/B = 13.80$ . B. P. water  $100.06^\circ$   
C. January 11, 1898.

*m*-Nitrobenzamide, 4.000 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, %.	$A-x$ .	$B-x$ .	$K$ .
30	5.28	67.7	18.99	27.8	1352	72.2	0.0197
60	10.27	77.1	21.66	47.4	1333	52.6	0.0197
90	15.92	91.7	25.76	61.8	1318	38.2	0.0198
120	14.04	70.0	19.66	71.4	1309	28.6	0.0194
150	16.29	73.4	20.62	79.0	1301	21.0	0.0194
180	15.71	65.7	18.46	85.1	1295	14.9	0.0198
210	13.90 <sup>1</sup>	53.9	15.14	88.9 <sup>2</sup>	1291	11.1	0.0197
240	21.82 <sup>1</sup>	82.6	23.20	91.9 <sup>2</sup>	1288	8.1	0.0198

Total variation = 2 per cent.  
of constant

Average constant = 0.0196

*m*-Nitrobenzamide (Old Way).

<i>t</i> .	Changed.	Unchanged.	Total.	Per cent. %.	
30	5.28	13.65	18.93	27.9	1352
60	10.27	11.30	21.57	47.6	1332
90	15.92	9.66	25.58	62.2	1318
120	14.04	5.54	19.58	71.7	1309
150	16.29	4.32	20.61	79.0	1301
180	15.71	2.76	18.47	85.1	1295
210	13.90 <sup>1</sup>	1.68	15.58 <sup>1</sup>	88.9 <sup>2</sup>	1291
240	21.82 <sup>1</sup>	1.87	23.69 <sup>1</sup>	91.9 <sup>2</sup>	1288

<sup>1</sup> Calculated from unchanged amide and total amide in sample.

<sup>2</sup> Some mistake.

Average constant = 0.0197

## SERIES VI.—Continued.

*p*-Nitrobenzamide, 4.000 grams.

On account of a precipitate which forms on cooling, 0.3 was deducted from the volume of each sample.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample, changed, <i>x</i> .	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	6.11	67.1	18.85	32.4	1348	67.6	0.0238
60	8.84	59.3	16.65	53.9	1326	46.1	0.0237
90	12.39	64.9	18.23	67.9	1312	32.1	0.0234
120	13.34	61.1	17.16	77.7	1302	22.3	0.0233
150	15.99	67.0	18.82	85.0	1295	15.0	0.0237
180	16.47	65.4	18.37	89.6	1290	10.4	0.0234
210	15.72	60.1	16.87	93.2	1287	6.8	0.0242
240	24.57	92.0	25.83	95.1	1285	4.9	0.0238

Average constant = 0.0236

*Benzamide*, 2.917 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample, changed, <i>x</i> .	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	5.21	64.6	18.12	28.7	1351	71.3	0.0204
60	9.91	72.8	20.45	48.5	1332	51.5	0.0203
90	12.55	70.2	19.72	63.6	1316	36.4	0.0208
120	14.14	69.1	19.41	72.9	1507	27.1	0.0202
150	13.69	59.9	16.82	81.4	1299	18.6	0.0210
180	15.94	67.1	18.85	84.6	1295	15.4	(0.0195)
210	18.02	70.8	19.90	90.6	1289	9.4	0.0212
240	24.21	92.3	25.92	93.4	1287	6.6	0.0214

Average constant = 0.0208





## SERIES VII.—Continued.

*o*-Methoxybenzamide, 2.426 grams in 500 cc. solution.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
60	5.80	66.3	18.63	31.1	1344	68.9	0.0114
120	7.77	52.2	14.66	53.0	1322	47.0	0.0115
150	11.71	67.0	18.82	62.2	1313	37.8	0.0120
180	13.72	71.5	20.08	68.3	1307	31.7	0.0119
210	10.47	51.5	14.47	72.3	1303	27.7	0.0114
240	15.94	77.0	21.63	73.7	1301	26.3	(0.0104)
270	21.06	93.0	26.12	80.6	1294	19.4	0.0116

Average constant = 0.0116

*o*-Toluic Amide, 2.712 grams in 500 cc. solution.

60	1.36	63.7	17.89	7.5	1368	92.5	0.00236
120	2.44	61.7	17.33	14.1	1361	85.9	0.00230
150	3.38	72.1	20.25	16.6	1358	83.4	0.00220
180	3.47	62.0	17.42	19.9	1355	80.1	0.00224
210	3.84	90.4	16.96	22.6	1352	77.4	0.00222
240	5.70	78.6	22.08	25.9	1349	74.1	0.00228
270.	6.96	88.8	24.95	27.9	1347	72.1	0.00221

Previous 0.00220  
Average constant =  
0.00224

## SERIES VIII.

HCl =  $A = 0.5494$  N.  $B = 0.02013$  N.  $A - B = 0.5293$ .  $A/B = 26.19$ . Bar. 769.8 mm. cor.  
 B. P. water  $100.35^{\circ}$  C. January 18, 1898.

*p*-Brombenzamide, 2.408 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	2.65	68.8	9.65	27.5	2592	72.5	0.0196
60	4.55	69.1	9.70	46.9	2572	53.1	0.0193
90	5.68	66.2	9.29	61.1	2558	38.9	0.0193
120	7.08	71.3	10.00	70.8	2548	29.2	0.0189
150	8.22	76.3	10.57	77.7	2541	22.3	0.0185
180	8.13	71.3	10.00	81.3	2538	18.7	0.0172
210	9.24	76.2	10.69	86.4	2533	13.6	0.0176
240	7.04	55.7	7.82	90.0	2529	10.0	0.0178
Previous 0.0146							
Average constant = 0.0185							

NOTE.—Owing to the fact that they are but slightly soluble, and that their acids are almost insoluble, the first two of these have given so much trouble, that half the usual concentrations were tried. This seems to affect the constant, as seen in the case of *p*-nitrobenzamide, 0.3 cc. on the bromamide, and 0.2 cc. on others, allowed on the volume of sample for precipitation.



## SERIES IX.

HCl =  $A = 0.5525$  N.  $B = 0.02013$ .  $A - B = 0.5324$ .  $A/B = 27.49$ . Bar. 764.5 mm. cor.  
 B. P. water  $100.16^{\circ}$  C. January 21, 1898.

*p*-Brombenzamide, 2.408 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> − <i>x</i> .	<i>B</i> − <i>x</i> .	<i>K</i> .
30	2.60	68.6	9.63	27.0	2722	73.0	0.0194
60	4.59	71.2	9.99	45.9	2703	54.1	0.0187
90	5.37	68.1	9.56	56.2	2691	43.8	0.0168
120	6.94	71.7	10.06	69.0	2680	31.0	0.0179
150	7.39	69.9	9.81	75.3	2674	24.7	0.0172
180	8.25	74.3	10.43	79.1	2670	20.9	0.0160
210	8.37	80.7	11.32	82.8	2666	17.2	0.0154
240	Distillation not complete.						
Average constant = 0.0173							

NOTE.—HCl in Series IX and X not titrated, but this is the usual value, and it is certainly close to the truth.

## SERIES IX.—Continued.

*m*-Brombenzamide, 2.408 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	2.93	70.2	9.86	29.7	2719	70.3	0.0214
60	4.73	65.9	9.25	51.1	2698	48.9	0.0218
90	6.00	65.9	9.25	64.9	2684	35.1	0.0214
120	7.87	73.5	10.32	76.3	2673	23.7	0.0221
150	9.07	79.8	11.20	82.8	2666	17.2	0.0217
180	9.15	73.7	10.38	88.2	2661	11.8	0.0220
210	9.35	71.8	10.08	92.7	2656	7.3	0.0231
240	11.67	87.9	12.34	94.6	2654	5.4	0.0226

Average constant = 0.0210

*p*-Chlorbenzamide, 1.872 grams.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .
30	2.51	65.5	9.20	27.3	2722	72.7	0.0193
60	4.25	63.1	8.86	48.3	2701	52.0	0.0199
90	6.23	71.1	9.98	62.4	2687	37.6	0.0200
120	7.42	71.8	10.08	73.6	2675	26.4	0.0204
150	8.99	80.0	11.23	80.1	2669	19.9	0.0199
180	7.89	65.7	9.23	85.5	2664	14.5	0.0198
210	8.54	68.9	9.68	88.2	2661	11.8	0.0188
240	10.68	82.2	11.54	92.6	2656	7.4	0.0201

Average constant = 0.0196



## SERIES X.

HCl =  $A = 0.5525$ .  $B = 0.04026$  N.  $A - B = 0.5122$ .  $A/B = 13.74$ . Bar. 752.7 cor. B. P. water  $99.73^{\circ}$  C.

*p*-Amidobenzamide, 3.280 grams.

$t$ .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent. changed, $x$ .	$A - x$ .	$B - x$ .	$K$ .
30	4.31	64.8	19.61	22.0	1352	78.0	(0.0151)
60	8.58	71.1	19.97	43.0	1341	57.0	0.0175
90	10.59	66.8	18.77	56.4	1318	43.6	0.0171
120	12.12	63.9	17.95	66.7	1307	33.3	0.0171
150	26.28	75.5	21.21	76.8	1297	23.2	0.0183
180	15.25	66.2	18.60	82.0	1292	18.0	0.0183
210	14.02	57.5	16.15	86.8	1287	13.2	0.0182
240	21.75	83.0	23.31	93.3	1281	6.7	(0.0214)

Average constant = 0.0177

*m*-Amidobenzamide, 37.12 grams.

30	4.31	63.6	17.87	24.1	1350	75.9	0.0167
60	8.51	70.5	19.84	42.4	1332	57.6	0.0169
90	10.39	65.1	18.29	56.3	1318	43.7	0.0171
120	Reading lost						
150	14.38	69.3	19.47	73.8	1300	26.2	0.0176
180	16.66	73.9	20.76	80.3	1294	19.7	0.0170
210	17.44	72.1	20.25	86.1	1288	13.9	0.0177
240	Distilling flask broke						

Average constant = 0.0170

## RECAPITULATION.

*Constant of Benzamide* = 0.0209.

<i>o</i> -Amido.	<i>o</i> -Chlor.	<i>o</i> -Iodo.	<i>o</i> -Nitro.		
0.00217	0.00305	0.00130	0.00073		
0.00194	0.00339	0.00119	0.00067		
0.00180	0.00320	0.00104	0.00050		
0.00167	0.00317	0.00108	0.00055		
0.00174	0.00315	0.00105	0.00058		
0.00178	0.00326	0.00111	0.00050		
0.00178	0.00327	0.00105	0.00055		
0.00174	0.00322	0.00106	0.00051		
0.00178	0.00321	0.00106	0.00054		
<i>o</i> -Toluic.	<i>o</i> -Toluic.	<i>o</i> -Hydroxy.	<i>o</i> -Hydroxy.	<i>o</i> -Methoxy.	<i>o</i> -Ethoxy.
0.00229	0.00236	0.00503	0.00463	0.0114	0.0092
0.00226	0.00230	0.00445	0.00458	0.0115	0.0091
0.00218	0.00220	0.00451	0.00432	0.0120	0.0094
0.00211	0.00224	0.00413	0.00436	0.0119	0.0093
0.00213	0.00222	0.00460	0.00433	0.0114	0.0095
0.00222	0.00228	0.00435	0.00439	(0.0104)	(0.0160)
0.00221	0.00221	0.00429	0.00440	0.0116	....
0.00222	....	0.00429	0.00440	....	....
0.00220	0.00224	0.00437	0.00437	0.0116	0.0093

Group.	Weight.	Constant of benz- amide—constant of ortho groups.	Retarda- tion. Per cent.
—CH <sub>3</sub>	15	0.0187	89.4
—NH <sub>2</sub>	16	0.0191	91.5
—OH	17	0.0164	79.1
—O.CH <sub>3</sub>	31	0.0093	44.1
—Cl	35.4	0.0177	84.6
—O.C <sub>2</sub> H <sub>5</sub>	45	0.0116	55.8
—NO <sub>2</sub>	46	0.0204	97.4
—I	127	0.0198	94.9

*Summary of Constants.*

Benz- amide.	Benz- amide.	<i>m</i> -Nitro.	<i>p</i> -Nitro.	$\frac{1}{2}$ conc. <i>p</i> -Nitro.	<i>m</i> -Amido.	<i>m</i> -Amido.
0.0200	0.0204	0.0197	0.0238	0.0255	0.0172	0.0167
0.0206	0.0203	0.0197	0.0237	0.0252	0.0178	0.0169
0.0211	0.0208	0.0198	0.0234	0.0254	0.0179	0.0171
0.0210	0.0202	0.0194	0.0233	0.0256	0.0176	....
0.0209	0.0210	0.0194	0.0237	(0.0276)	0.0184	0.0167
0.0219	(0.0195)	0.0198	0.0234	0.0248	0.0172	0.0170
0.0211	0.0212	0.0197	0.0242	0.0238	0.0183	0.0177
....	0.0214	0.0198	0.0238	(0.0275)	0.0171	....
0.0209	0.0208	0.0196	0.0236	0.0256	0.0177	0.0170

<i>p</i> -Amido.	<i>p</i> -Amido.	<i>p</i> -Chlor.	$\frac{1}{2}$ conc. <i>p</i> -Chlor.	$\frac{1}{2}$ conc. <i>p</i> -Chlor.	<i>m</i> -Brom.
0.0180	(0.0151)	0.0170	(0.0221)	0.0193	0.0151
0.0187	0.0175	0.0181	0.0205	0.0199	0.0179
0.0190	0.0171	0.0183	0.0208	0.0200	0.0190
0.0195	0.0171	0.0180	0.0203	0.0204	0.0192
0.0204	0.0183	0.0175	0.0197	0.0199	0.0200
0.0218	0.0183	....	0.0202	0.0198	0.0199
0.0214	0.0182	0.0189	0.0204	0.0188	0.0179
....	(0.0214)	0.0172	0.0209	0.0201	....
<hr/>					
0.0198	0.0177	0.0179	0.0204	0.0196	0.0184
$\frac{1}{2}$ conc. <i>m</i> -Brom.	<i>p</i> -Brom.	$\frac{1}{2}$ conc. <i>p</i> -Brom.	$\frac{1}{2}$ conc. <i>p</i> -Brom.	<i>m</i> -Toluic.	<i>p</i> -Toluic.
0.0214	0.0140	0.0196	0.0194	0.0181	0.0168
0.0218	0.0161	0.0193	0.0187	0.0183	0.0173
0.0214	0.0157	0.0193	0.0168	0.0191	0.0170
0.0221	0.0154	0.0189	0.0179	0.0193	0.0175
0.0217	0.0147	0.0185	0.0172	0.0196	0.0172
0.0220	0.0141	0.0172	0.0160	0.0195	0.0182
0.0231	0.0135	0.0176	0.0154	0.0204	0.0176
0.0226	0.0131	0.0178	....	0.0200	(0.0196)
<hr/>					
0.0210	0.0146	0.0186	0.0173	0.0193	0.0175

## DISCUSSION OF RESULTS.

*Experiments, Group I.*—Series 1, 2, 3, and 4 with hydrochloric acid show very clearly that *o*-nitrobenzamide yields extremely slowly to the action of the acid while the meta is readily hydrolyzed and the para still more so. The constants obtained for the meta and para do not vary specially with different concentrations of the acid. The variations in the constants found may be due to changes of barometric pressure. As a very dilute acid is much more completely dissociated it would be expected to give a higher constant. The ammonium salt formed certainly retards the reaction, comparatively, much more with a weak than with a strong acid. These two opposite effects may balance and keep the actual velocity very nearly the same.

Series 5, 6, and 7 indicate that the relations between the meta- and paranitrobenzamides are approximately the same with sulphuric acid as with hydrochloric acid. The results, though not quite comparable, show that the sulphuric acid is

about 0.45 times as strong as hydrochloric. Should one wish to compare the strengths of acids by measuring the rates at which they hydrolyze a given amide it seems that it would be proper to divide the average constant found in a series with one by the similar average constant found with the other, the conditions under which the measurements were made being the same. Some years ago Ostwald<sup>1</sup> in his elaborate studies on the hydrolysis of acetamide, arbitrarily, as he says, estimated the strengths of a number of acids from the time it took them to hydrolyze 50 per cent of the acetamide.

*Experiments, Group II.*—In Series I the caustic soda was made by adding sodium to water. The results show a high but decreasing constant. In Series II the alkali was made by adding barium hydrate to an approximately  $\frac{N}{10}$  solution of pure sodium sulphate. The large excess of sodium sulphate seems to have retarded the reaction. The slowing up of the reaction due to formation of neutral salts in addition to that already in solution appears also in Series III and IV; in the latter the metaamide does not seem to have gone into solution quickly. In Series V neither seems to have started promptly, which gives to the reaction the appearance of acceleration. Sometimes it is difficult to induce substances to dissolve as quickly as it is desirable for such work even though more than enough of the solvent is present. Series VI gave a good constant for the meta. The para could not be trusted to dissolve readily enough at this temperature. The few determinations here made with benzamide do not warrant any conclusions.

Series VIII and IX with caustic potash, which was likewise prepared from potassium sulphate and barium hydrate, practically duplicate the corresponding ones with caustic soda. In Series VIII it was known that the meta did not dissolve quickly, which accounts for the low value of the constant at first.

Series X and XI with barium hydrate gave much higher constants than those with either caustic soda or potash. This is attributable to the absence of the neutral salt. The salt which was formed during the reaction retards it very markedly. The great influence of the neutral salts was not realized until these experiments were made, otherwise the excess

<sup>1</sup> J. prakt. Chem. (2) 35, 112.

of sodium and potassium sulphate in the previous series would have been avoided.

*Influence of Temperature.*—The presence of sodium sulphate in the experiments with caustic soda deprive the results of much of their value, but as about the same amount was present in each case some conclusions may be drawn as to the relative velocities at different temperatures. For *m*-nitrobenzamide the average constants found were :

60°.	70°.	80°.	90°.	100°.
0.058	0.107	0.184	0.305	0.485

The values were plotted and the constants for intermediate degrees estimated from the curve. When this series of values was examined its members were found to be very nearly the geometrical progression. A geometrical series was calculated, assuming 0.058 and 0.485 as extremes. The two are here given.

60°.	70°.	80°.	90°.	100°.	
0.058	0.107	0.184	0.305	0.485	Experiment
0.058	0.099	0.168	0.285	0.485	Calculated

The agreement is as close as could be expected considering the known errors of the constants. Such a law as this would make it easy to compare results obtained at temperatures not too far apart, such, for instance, as the temperature of boiling water under various atmospheric pressures. It is intended to make and use such a temperature curve for reducing to "standard conditions" the results of the various experiments of Group III.

Van 't Hoff and others have shown that the variation of the constant for temperature should be of the form

$$\frac{dl. k}{dT} = \frac{A}{T^2} + B,$$

in which  $T$  is absolute temperature and  $A$  and  $B$  are quantities depending on the nature of the reaction.

Berthelot has shown in esterification experiments that in this expression  $A$  may be 0 when it takes the form  $K = ab^t$ , which agrees exactly with the conclusion reached above.

The few experiments made with *o*-nitrobenzamide show

that it resists hydrolysis by caustic soda about as well as it resists the influence of the acid.

*Experiments, Group III.*—The experiments with the various amides studied were made under as nearly the same conditions as convenient, so that the results should be more directly comparable. The earlier results are, of course, not quite so good as those obtained later. It is regretted that in so many instances numbers occur which are out of harmony with their environment. These are due to various causes, sometimes to mistakes in measuring the samples, or in reading burettes, and sometimes to causes unknown. In making up the average results the liberty was taken of throwing out figures evidently erratic.

*p*-Amidobenzamide has so far failed to give satisfactory results. It was hard to get the distillate to come over neutral, and there seems to be something in it which interferes with the end-reaction in titrating. *p*-Chlor- and *p*-brombenzamides went into solution slowly and as the corresponding acids were formed they crystallized out even at 100° C., and seemed to bring down some of the amides with them. This led to several series in which half quantities were used. Those gave much higher and, in general, better results, but here analytical difficulties were much increased, as complete decomposition gave only 20 mg. ammonia in many cases. Even 1 per cent of this amount is rather a small amount of ammonia. The results obtained in a similar series with *p*-nitrobenzamide were about 4 per cent higher than those at the ordinary concentration even after allowing for the unusually high barometer. The cause of this is not yet known.

The possibilities of the method may be judged from the experiments with *m*-nitrobenzamide in Series VI, according to the new method, in which the total variation is only 2 per cent of the value of the constant. This variation in the constant may be accounted for by an error of several tenths of a per cent in the analyses.

#### CONCLUSIONS.

The results obtained with the meta- and para-substituted benzamides go to show that groups in these positions usually exercise some, though not a very marked retarding influence

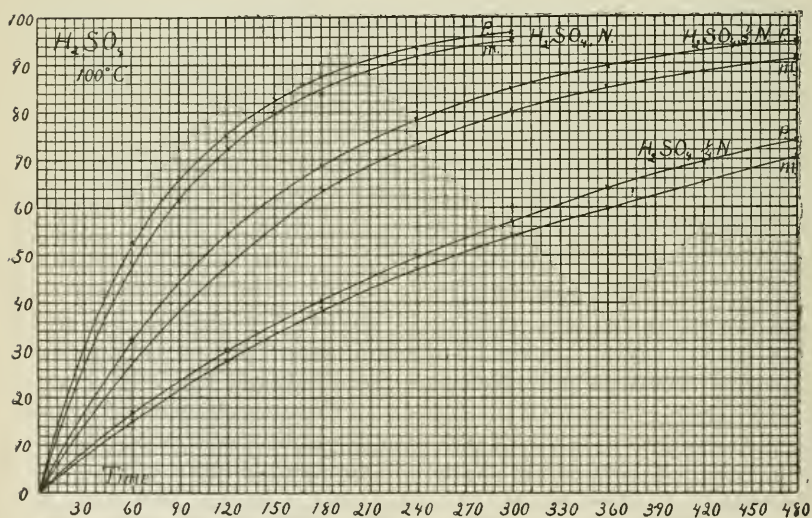
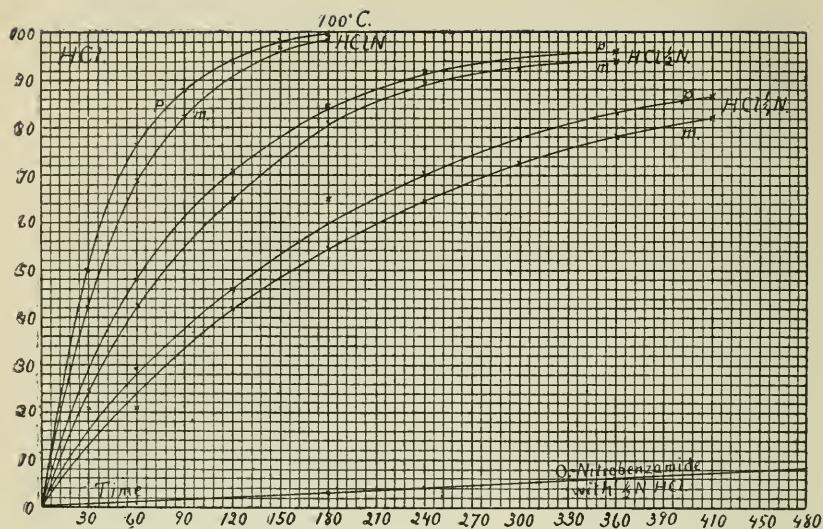


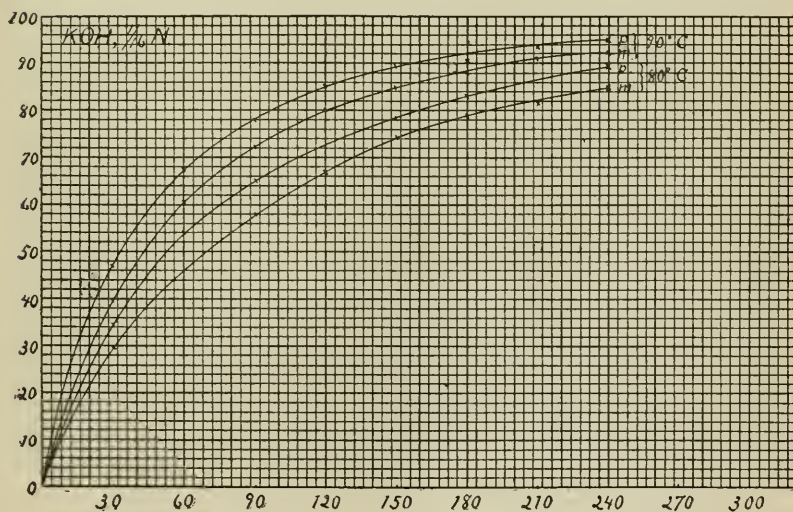
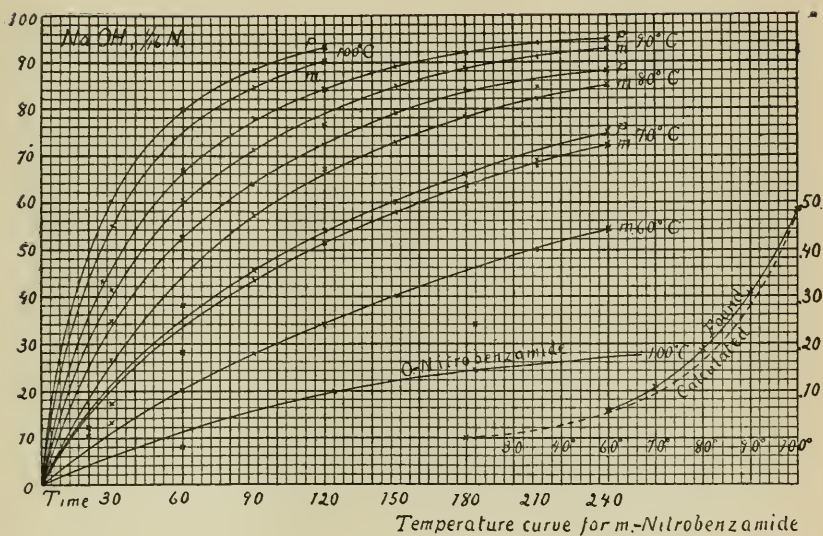
on the rate of hydrolysis. The rate does not seem to vary inversely as the molecular weight as Kellas concludes from his experiments on the etherification of meta-substituted benzoic acids. The nitro-group in the para position causes a very marked increase in the speed of hydrolysis.

The experiments with ortho-substituted benzamides all show that groups in this position exert a remarkable "protective" influence on the amide group. With similar groups this influence varies roughly with the weight of the group but otherwise it seems to depend more upon the nature than the weight of the group. For instance, methyl with a weight of 15 protects far better than chlorine, or even than the methoxy group  $\text{—OCH}_3$ . The nitro-group is remarkable in its protective power, for though it has a weight of only 46 it "protects" more than twice as much as iodine (126). The methoxy and ethoxy groups are remarkable on account of their slight influence—far less than that of hydroxyl.

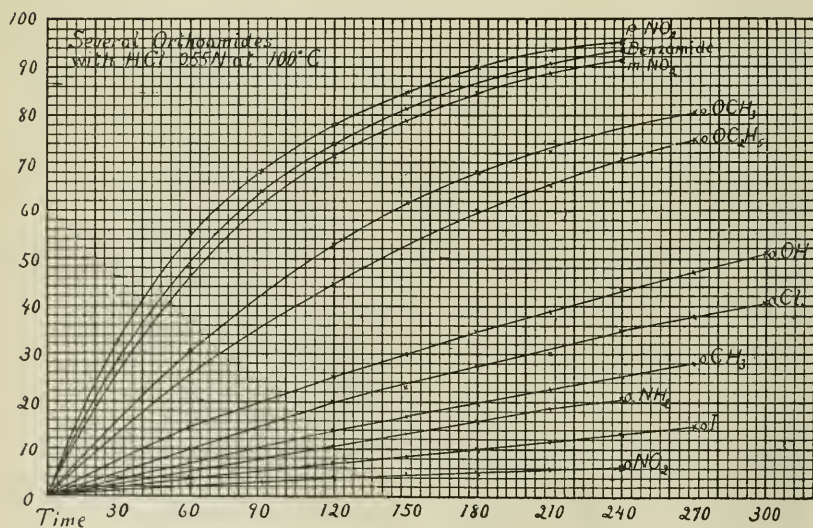
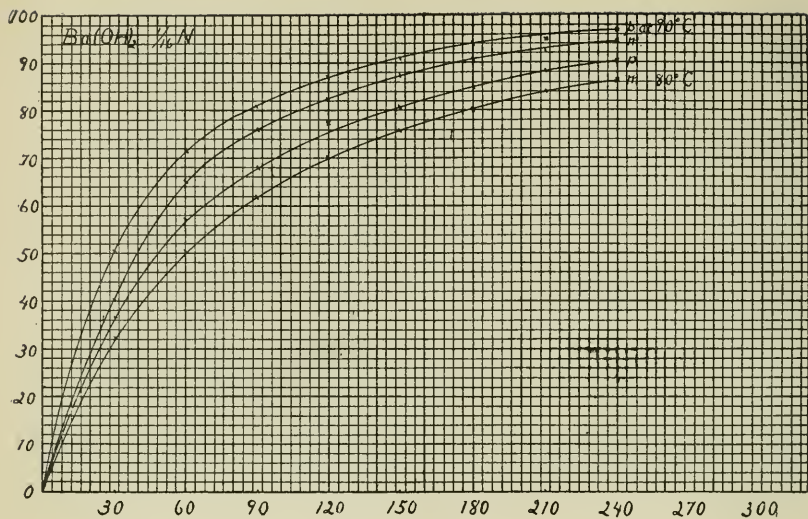
The general results reached by V. Meyer, Sudborough, Kellas, and others on the rate of formation of ethereal salts are generally in harmony with those here found, except that in the formation of ethereal salts the weight of the group seems to be of far more importance than its nature. Kellas found the nitro-group in the ortho position to have an exceptional retarding influence. The two lines of investigation seem entirely analogous and, when they have been more thoroughly worked out, it will be interesting to compare the results. The study of the hydrolysis of amides seems to have many advantages over the other. The experiments are so much simpler, and the reactions are better understood and are generally freer from complications. The reaction does not take place at such low temperatures as does the formation of ethereal salts. The possibility of using water solutions is no small advantage. The greatest advantage is a simple and direct method of analysis. Many of the results recorded in this article are brought together graphically in curves.

In a subsequent article some further results with these amides and with several others will be given, as well as the results of the study of the hydrolysis of these amides with alkali.









CHEMICAL LABORATORY,  
JOHNS HOPKINS UNIVERSITY,  
February, 1899.

## ALIPHATIC SULPHONIC ACIDS.

### III.—(1)-BROMETHYLENESULPHONIC ACID.

BY ELMER P. KOHLER.

Bromine reacts with ethylenesulphonic acid to form a monobrom substitution-product. In a previous paper<sup>1</sup> I showed that this is probably (1)-bromethylenesulphonic acid,  $\text{CH}_2=\text{CBrSO}_3\text{H}$ . This formula has since been definitely established by transforming the substance into bromsulphoacetic

acid,  $\text{CHBr} \begin{cases} \text{COOH} \\ \text{SO}_3\text{H} \end{cases}$ . This acid can only be formed from one

in which the bromine atom and the sulphonic acid group are in combination with the same carbon atom.

This paper contains an account of the results obtained by a study of (1)-bromethylenesulphonic acid, and of those acids which are formed from it by direct addition of other substances. The material is presented under the following heads:

I. (1)-Bromethylenesulphonic acid.

II. (1,2)-Bromoxyethanesulphonic acid.

III. (1,2)-Dibromethanesulphonic acid.

IV. Acids formed by the action of sulphuric acid on bromethylenesulphonic acid.

#### I. (1)-BROMETHYLENESULPHONIC ACID.

*Preparation.*—An aqueous solution of the acid is obtained by liberating it from the lead salt,<sup>2</sup> filtering, and removing the excess of hydrogen sulphide by boiling. In dilute aqueous solution the acid is quite stable; after boiling a solution containing approximately 6 grams of acid in 100 cc. of solution, for five hours, it gave only a faint reaction for hydrobromic acid and no reaction for sulphuric acid. On neutralizing with potassium carbonate, evaporating to dryness, and extracting with 95 per cent alcohol only 0.4 gram of material insoluble in alcohol was obtained. This was the potassium salt of (1,2)-bromoxyethanesulphonic acid described below.

<sup>1</sup> This JOURNAL, 20, 694.

<sup>2</sup> *Ibid.*, 20, 693.

The alcoholic solution was evaporated to dryness and the residue analyzed. It contained 17.1 per cent potassium instead of 17.33 per cent calculated for  $C_2H_4BrSO_3K$ . On boiling the aqueous solution, therefore, there is no change except an exceedingly slow addition of water. If, however, the aqueous solution is evaporated on the water-bath or in a vacuum, over phosphorus pentoxide, a point is reached beyond which it is impossible to concentrate it without decomposing the acid. The liquid becomes dark in color, hydrobromic acid and sulphur dioxide are split off, and there is left a pasty mass from which no pure substances were obtained. As ether does not extract the acid from its solution in water, the pure acid could not be isolated.

*Salts.*—The salts were prepared by neutralizing cold solutions of the acid with carbonates or oxides. All the salts are extremely soluble in water, most of them are hygroscopic, and only the salts with the alkali metals crystallize well. Only the potassium, sodium, and barium salts were analyzed.

The potassium salt was described in an earlier paper, where a complete analysis is given.

The sodium salt, crystallized from absolute alcohol, washed with ether, and dried at  $50^\circ$ , gave the following results on analysis:

I. 0.1510 gram salt gave 0.0522 gram  $Na_2SO_4$ .

II. 0.1488 gram salt gave 0.0512 gram  $Na_2SO_4$ .

Na	Calculated for $C_2H_4BrSO_3Na$ .	Found.	
	I I	I.	II.
		11.2	11.15

The salt is deliquescent and cannot be crystallized from water. It is readily soluble in ordinary alcohol, difficultly soluble in absolute alcohol, insoluble in ether. From alcohol it crystallizes in long, flat needles.

The barium salt crystallizes from water in long hygroscopic needles, which lose water and crumble as soon as they are removed from the mother-liquors. From the concentrated aqueous solution absolute alcohol precipitates an anhydrous salt in small needles.

I. 0.1794 gram salt gave 0.0820 gram  $BaSO_4$ .

II. 0.2012 gram salt gave 0.0926 gram  $BaSO_4$ .



	Calculated for $C_2H_2BrSO_3Ba$ .	I.	Found. II.
Ba	27.02	26.9	27.1

The salt is readily soluble in water, insoluble in absolute alcohol.

(1)-Bromethylenesulphone Chloride.

The dry potassium salt reacts with phosphorus pentachloride in the cold. Under these conditions, however, very little sulphone chloride is obtained, as the reaction goes too far, the sulphonic acid group being replaced by chlorine. A better yield of chloride was obtained by adding the pentachloride to the finely powdered potassium salt suspended in chloroform, and boiling until all the salt was transformed. The chloroform and chlorides of phosphorus were removed by distillation under diminished pressure, the residue repeatedly washed with ice-water, and dried in a vacuum over phosphorus pentoxide.

I. 0.2820 gram chloride gave 0.1977 gram AgCl.

II. 0.2212 gram chloride gave 0.1551 gram AgCl.

	Calculated for $C_2H_2BrClSO_2$ .	I.	Found. II.
Cl	17.11	17.4	17.4

The chloride is an oily liquid which cannot be distilled without decomposition, even in a vacuum. It does not solidify at  $-20^\circ$ . When boiled with water it passes back into the acid, not a trace of sulphur dioxide or hydrobromic acid being split off.

Oxidation of (1)-Bromethylenesulphonic Acid.

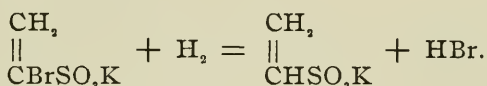
The acid behaves towards oxidizing agents like ethylene-sulphonic acid. Potassium permanganate, silver oxide, nitric acid, and barium manganate were tried. The products in all cases were carbon dioxide, sulphuric acid, hydrobromic acid, and water.

Reduction.

The acid is easily reduced. Even on boiling the neutral solution of the potassium salt with zinc or magnesium powder the bromine is slowly replaced by hydrogen. In the presence of free acid the reduction is much more rapid. In either case,

however, it stops with the formation of ethylenesulphonic acid and is quantitative.

An excess of zinc powder was added to 10 grams of the potassium salt, dissolved in 100 cc. of water, the solution heated to boiling, and hydrochloric acid added, drop by drop, until all the zinc was dissolved. The liquid gave no reaction for sulphide, sulphite, or sulphate, showing that the sulphonic acid group had been left intact. The zinc was removed with ammonium sulphide, the ammonium chloride and bromide with lead oxide, the liquid evaporated to dryness, and the residue extracted with alcohol. It gave 6.1 grams of pure potassium ethylenesulphonate instead of 6.5 grams calculated according to the equation :



*Replacement of Bromine by Double Decomposition.*

The ease with which hydrogen is substituted for the bromine suggested the possibility of replacing it by double decomposition. Many experiments were made in this direction, but, with one exception, all were unsuccessful. The acid reacts only with substances which, like potassium cyanide, have an alkaline reaction. These invariably split off the sulphonic acid group along with the bromine. The one exception is the reaction with mercuric chloride. When an alkaline solution of the potassium salt is boiled with a large excess of mercuric chloride the bromine is slowly replaced with chlorine. After removing the mercury and halogen in the usual way a potassium salt is obtained which crystallizes from alcohol in small plates.

I. 0.1814 gram salt gave 0.0876 gram  $\text{K}_2\text{SO}_4$ .

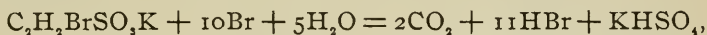
II. 0.2265 gram salt gave 0.1087 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_2\text{H}_2\text{ClSO}_3\text{K}$ .	I.	Found.	II.
K	21.61	21.6		21.5

*Behavior towards Halogens.*

As an unsaturated acid, bromethylenesulphonic acid is capable of combining with other substances. It is not possi-

ble, however, to add the halogens or hypochlorous acid. In aqueous solution the acid and its salts slowly react with bromine, but the result is oxidation. Carbon dioxide is given off and sulphuric acid is found in the solution. Two grams of the potassium salt reacted with 7.4 grams of bromine. The equation,



requires 7.1 grams of bromine for 2 grams of salt. On evaporating to dryness, the residue was found free from organic matter. In aqueous solution, therefore, bromine oxidizes the acid to carbon dioxide and water.

Chlorine and hypochlorous acid react in the same way, oxidizing the substance rapidly at  $0^\circ$ . Iodine has no action.

To avoid the presence of water a solution of the acid in acetic acid was prepared as follows: An aqueous solution of the acid was concentrated, as far as possible, in a vacuum. The amount of sulphonic acid present per gram of this solution was determined by neutralizing with standard base. The solution was then mixed with glacial acetic acid and the quantity of acetic anhydride, calculated to combine with all the water present, added. This solution does not react with bromine below  $80^\circ$ . At this temperature the bromine attacks both the unsaturated acid and the solvent. The result is a mixture which was not separated. It was found, however, that the reaction with the unsaturated acid was addition, as the solution contains no sulphuric acid, and the amount of hydrobromic acid formed is only a small fraction of the amount calculated for substitution.

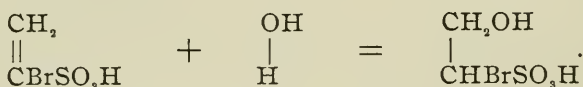
#### *Addition of Water.*

(1)-Bromethylenesulphonic acid combines with water more readily even than ethylenesulphonic acid. On simply boiling aqueous solutions of the acid or its salts there is a slow combination with water. At  $120^\circ$  a ten per cent solution of the acid passes quantitatively into bromethylenesulphonic acid in less than three hours. In the presence of a small quantity of an alkaline carbonate or an inorganic acid the addition takes place on the water-bath. If, for example, the solution ob-

tained by treating a solution of ethylenesulphonic acid with bromine, is concentrated on the water-bath and then neutralized, very little salt of the unsaturated acid is obtained,—in the presence of the hydrobromic acid the unsaturated acid passes into the oxy-acid while the solution is being concentrated. Alcohol and many soluble salts similarly favor the addition. In fact, in nearly all the experiments with the acid, some is lost in this way.

## II. (1,2)-BROMOXYETHANESULPHONIC ACID.

It will be shown below that the acid formed by the addition of water to (1)-bromethylenesulphonic acid is (1,2)-bromoxyethanesulphonic acid.



The acid itself could not be obtained in crystalline condition, hence it was not analyzed. The salts were obtained by adding water to the salts of bromethylenesulphonic acid. They are easily separated from the latter as they are insoluble in alcohol and crystallize well from water.

*Salts.*—The sodium salt crystallizes from water in very characteristic conical aggregates.

I. 0.2455 gram salt lost 0.0095 gram  $\text{H}_2\text{O}$  at  $130^\circ$ .

II. 0.3135 gram salt lost 0.0115 gram  $\text{H}_2\text{O}$  at  $130^\circ$ .

III. 0.4224 gram anhydrous salt gave 0.1630 gram  $\text{CO}_2$ , and 0.0722 gram  $\text{H}_2\text{O}$ .

IV. 0.2360 gram anhydrous salt gave 0.0730 gram  $\text{Na}_2\text{SO}_4$ .

V. 0.3026 gram anhydrous salt gave 0.094g gram  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{C}_2\text{H}_4\text{BrSO}_4\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$ .	Found.		
$\text{H}_2\text{O}$	3.8	I.	3.8	II.
	Calculated for $\text{C}_2\text{H}_4\text{BrSO}_4\text{Na}$ .	III.	Found IV.	V.
C	10.6	10.4	....	....
H	1.8	1.9	....	....
Na	10.1	...	10.2	10.1

The potassium salt crystallizes from water in small lustrous prisms. The air-dried salt contains 0.5 molecule of water, which it loses below  $150^\circ$ .

I. 0.3269 gram salt lost 0.0125 gram  $\text{H}_2\text{O}$ .

II. 0.2666 gram salt lost 0.0103 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_2\text{H}_4\text{BrSO}_4\text{K} \cdot \frac{1}{2}\text{H}_2\text{O}$ .	I.	Found.	II.
$\text{H}_2\text{O}$	3.6	3.8		3.8

I. 0.3150 gram anhydrous salt gave 0.1147 gram  $\text{K}_2\text{SO}_4$ .

II. 0.2564 gram anhydrous salt gave 0.0103 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_2\text{H}_4\text{BrSO}_4\text{K}$ .	I.	Found.	II.
K	16.05	16.3		16.15

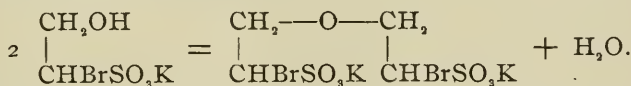
When the anhydrous potassium salt is heated in an oil-bath it melts at about  $200^\circ$  and begins to lose water a few degrees above this point. If the temperature is kept constant at  $225^\circ$  until the weight is constant, the loss is 4.2 per cent, which is somewhat more than 1 molecule of water for 2 molecules of salt. The amber-colored residue contains traces of bromide and sulphite. It does not react with bromine, and therefore contains no unsaturated acid. From the aqueous solution alcohol precipitates the potassium salt of dibromdiisethionic acid in thin flakes.

I. 0.2022 gram salt gave 0.0758 gram  $\text{K}_2\text{SO}_4$ .

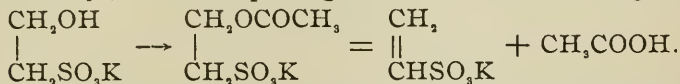
II. 0.2212 gram salt gave 0.0834 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_4\text{H}_6\text{Br}_2\text{S}_2\text{O}_7\text{K}_2$ .	I.	Found.	II.
K	16.66	16.8		16.9

The salts of bromoxyethanesulphonic acid therefore behave like isethionates when heated :



I found it possible to pass from isethionic acid to the unsaturated ethylenesulphonic acid by first replacing the hydroxyl with acetyl, and then splitting off acetic acid by heating.<sup>1</sup>



The same reaction was tried with bromoxyethanesulphonic acid. The potassium salt was heated in an oil-bath with an

<sup>1</sup> This JOURNAL, 20, 683.

excess of acetic anhydride until a clear liquid was obtained. The excess of the anhydride was removed with absolute alcohol and the residue recrystallized from ordinary alcohol. The potassium salt of (1,2)-bromacetoxyethanesulphonic acid was thus obtained in small lustrous needles, readily soluble in water, difficultly soluble in boiling alcohol.

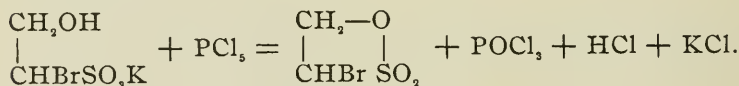
0.3337 gram salt gave 0.1065 gram  $K_2SO_4$ .

	Calculated for $C_4H_6BrSO_4K$ .	Found.
K	14.08	14.3

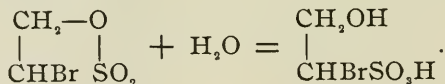
When this salt was heated in an oil-bath it remained unchanged until the temperature was nearly  $300^\circ$ . At this point acetic acid or acetic anhydride is given off, but the salt begins to turn black and no unsaturated acid can be isolated from the residue.

*Reaction with Phosphorus Pentachloride.*

The dry potassium salt of bromoxyethanesulphonic acid reacts so readily with phosphorus pentachloride that unless the mass is well cooled with ice-water the liquid becomes black. On pouring the product into ice-water a thick liquid is obtained which cannot be freed from phosphorus by washing and which contains only a small amount of chlorine. It slowly goes into solution in cold water. This solution contains (1,2)-bromoxyethanesulphonic acid as the only organic product. The substance is probably a sulpholactone formed according to the equation :



This reacts with water to form the oxy-acid :

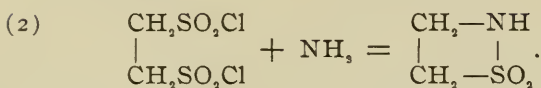
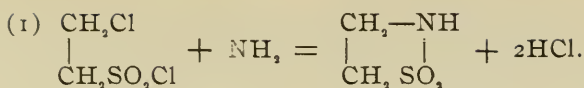


A corresponding nitrogen compound has been obtained from (2)-chloroethanesulphone chloride<sup>1</sup> and from (1,2)-ethanedithione chloride.<sup>2</sup>

<sup>1</sup> J. prakt. Chem. [2], 20, 383.

<sup>2</sup> This JOURNAL, 19, 746.





I have obtained similar lactones with the higher members of the oxysulphonic acids, and in a later paper I expect to show that the sulpholactone ring closes quite as readily in the  $\beta$ - as in the  $\gamma$ -position.

If the same potassium salt is suspended in chloroform and then treated with phosphorus pentachloride, the reaction takes place slowly and the product is colorless. After distilling off the chloroform and chlorides of phosphorus under diminished pressure and washing with ice-water, an oily liquid is obtained which, when dried in a vacuum over phosphorus pentoxide, has approximately the composition of chlorbromethanesulphone chloride.

I. 0.1850 gram substance, decomposed with water, gave 0.1118 gram AgCl.

II. 0.2125 gram substance gave 0.1325 gram AgCl.

	Calculated for $\text{C}_2\text{H}_2\text{ClBrSO}_2\text{Cl}$ .	I.	Found.
			II.
Cl	14.62	15.0	15.1

The high percentage of chlorine is due to a small quantity of phosphorus oxychloride, which could not be removed without series loss of substance.

This chloride was decomposed with water and the product isolated in the form of the sodium salt, by the method previously described with other chlorides. The sodium salt, crystallized from alcohol and dried at  $100^\circ$  gave the following analytical results:

I. 0.4251 gram salt gave 0.1496 gram  $\text{CO}_2$ , and 0.535 gram  $\text{H}_2\text{O}$ .

II. 0.5211 gram salt gave 0.1815 gram  $\text{CO}_2$ , and 0.0657 gram  $\text{H}_2\text{O}$ .

III. 0.1621 gram substance gave 0.2176 gram AgCl, AgBr.

IV. 0.1323 gram substance gave 0.1820 gram AgCl, AgBr.

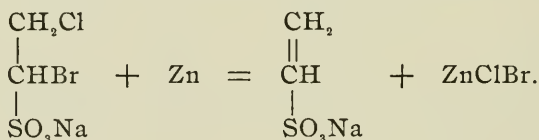
V. 0.5127 gram salt gave 0.1425 gram  $\text{Na}_2\text{SO}_4$ .

VI. 0.3049 gram salt gave 0.0875 gram  $\text{Na}_2\text{SO}_4$ .

	Calculated for $C_2H_3O_3SClBrNa$ .	I.	II.	Found.		V.	VI.
C	9.77	9.6	9.5	...	...	..	..
H	1.22	1.4	1.5	...	...	..	..
Cl.Br	47.04	..	..	46.9	47.3	..	..
Na	9.36	..	..	...	...	9.2	9.2

When a dibromcarbonic acid, in which the two bromine atoms are in combination with adjoining carbon atoms, is reduced with zinc and acid, the two halogen atoms are eliminated, and an unsaturated acid is formed. It was of interest, therefore, to determine whether an analogous dihalogensulphonic acid would behave in the same way, as this would give a method for determining the structure of halogensulphonic acids and a new way of passing from an oxy to an unsaturated acid.

Twenty grams of the sodium salt described above were dissolved in water and boiled with zinc powder until no more zinc went into solution. The reduction took about five hours. The zinc and halogen were removed in the usual way, the solution evaporated to dryness, and the residue recrystallized from alcohol. 9.5 grams of sodium salt were obtained instead of 10.6 grams calculated according to the equation :



A sodium determination gave 17.8 per cent sodium instead of 17.6 per cent calculated for  $C_2H_3SO_3Na$ . The behavior towards permanganate and bromine was the same as that of ethylenesulphonic acid salts prepared in other ways. The behavior of these dihalogensulphonic acids towards zinc is therefore exactly the same as that of the corresponding carbonic acids.

*Reduction of (1,2)Bromoxyethanesulphonic Acid.*

It is much more difficult to reduce this acid than the one from which it is obtained by addition of water. An aqueous solution of the sodium salt was boiled with zinc powder for hours without getting a trace of zinc bromide into solution.

On adding dilute sulphuric acid and continuing to boil the bromine was slowly replaced, but the amount of zinc required was so large that it was difficult to isolate the reduction-product. With 2 per cent sodium amalgam and dilute sulphuric acid, however, the reduction was satisfactory. After removing the mercury most of the sodium sulphate was precipitated with alcohol, the filtrate from this evaporated to dryness, and the residue extracted with 90 per cent alcohol. From the alcoholic solution, on cooling, the sodium salt of oxyethanesulphonic acid separated in plates.

I. 0.1188 gram salt gave 0.0561 gram  $\text{Na}_2\text{SO}_4$ .

II. 0.1660 gram salt gave 0.0782 gram  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{C}_2\text{H}_5\text{SO}_3\text{Na}$ .	I.	Found.	II.
Na	15.54	15.3		15.2

With phosphorus pentachloride this salt gave a chloride boiling at  $200^\circ$ , the boiling-point of (2)-chlorethanesulphone chloride. The salt is, therefore, sodium isethionate. This proves that in bromoxyethanesulphonic acid the hydroxyl and sulfoxyl groups are in the (1,2)-relation.

#### *Oxidation.*

Potassium permanganate oxidizes bromoxyethanesulphonic acid to carbon dioxide, water, hydrobromic acid, and sulphuric acid.

Ten grams of the potassium salt were warmed with the quantity of the normal permanganate solution required to oxidize the salt to bromsulphoacetic acid. When the color of permanganate had disappeared the liquid was neutral to litmus and gave reactions for carbonate, bromide, and sulphate. On concentrating it a considerable quantity of unoxidized salt crystallized out. No other organic compound was found. With weak acid permanganate the oxidation was slower but the products were the same.

Concentrated nitric acid oxidizes to oxalic acid.

The acid does not attack the substance in the cold. On warming the mixture on the water-bath all the sulphur is split off as sulphuric acid. On concentrating the strongly acid liquid on the water-bath and allowing to cool, oxalic acid

crystallizes out. Nitric acid leaves the carbon skeleton intact.

Silver oxide oxidizes to glycolic acid.

In hot aqueous solutions the acid rapidly reduces freshly precipitated silver oxide. Silver sulphate goes into solution while metallic silver, silver bromide, and an organic silver salt separate out. A quantity of this precipitate was digested with hydrochloric acid and the solution repeatedly extracted with ether. From the ethereal solution, on evaporation, a small quantity of a carbonic acid crystallized in thin plates melting at  $78^{\circ}$ . Analysis and properties showed that the substance is glycolic acid.

0.2820 gram substance gave 0.3247 gram  $\text{CO}_2$ , and 0.1345 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_2\text{H}_4\text{O}_3$ .	Found.
C	31.6	31.4
H	5.3	5.3

Barium manganate oxidizes to bromsulphoacetic acid.

It is evident that in all the above oxidations one of the changes is the replacement of bromine by hydroxyl thus forming an extremely unstable oxysulphonic acid. To avoid this it is necessary to have a perfectly neutral oxidizer, one that can be kept neutral during oxidation. Such a substance was finally found in barium manganate. If a current of carbon dioxide is passed into water in which barium manganate is suspended, barium carbonate is precipitated and the manganate passes into the permanganate. If an oxidizable substance is present, the permanganate is reduced as fast as formed, the barium being precipitated as carbonate while the manganese is precipitated in the form of hydrated oxides. The reaction therefore always remains neutral.

Ten grams of the potassium salt of bromoxyethanesulphonic acid were dissolved in 250 cc. of water, an excess of barium manganate added, and a current of carbon dioxide passed into the liquid until a permanent purple color of permanganate remained. The solution was then decolorized with a little alcohol, filtered, and the potassium removed with sulphuric acid and alcohol. The resulting liquid was heated to boil-

ing, neutralized with barium carbonate, and filtered. On cooling, a difficultly soluble barium salt crystallized out in colorless needles. An analysis of the air-dried salt gave the following results :

- I. 0.2110 gram substance lost 0.0200 gram at  $130^{\circ}$ .
- II. 0.2008 gram substance lost 0.0188 gram.
- III. 0.2220 gram substance gave 0.1245 gram  $\text{CO}_2$ , and 0.0234 gram  $\text{H}_2\text{O}$ .
- IV. 0.6552 gram substance gave 0.1585 gram  $\text{CO}_2$ , and 0.0236 gram  $\text{H}_2\text{O}$ .
- V. 0.2245 gram substance gave 0.1200 gram AgBr.
- VI. 0.2112 gram substance gave 0.1134 gram AgBr.
- VII. 0.1820 gram substance gave 0.1197 gram  $\text{BaSO}_4$ .
- VIII. 0.2001 gram substance gave 0.1395 gram  $\text{BaSO}_4$ .

		Calculated for C <sub>2</sub> HBrO <sub>5</sub> SBa.2H <sub>2</sub> O.		I.		Found.	
H <sub>2</sub> O		9.24		9.I		9.2	
		Calculated for C <sub>2</sub> HBrO <sub>5</sub> SBa.		Found.			
		III.	IV.	V.	VI.	VII.	VIII.
C	6.77	6.5	6.6	...	...	...	...
H	0.28	0.5	0.4	...	...	...	...
Br	22.6	..	..	22.8	22.9	...	...
Ba	38.7	..	..	...	...	38.7	38.5

The salt was easily reduced with 2 per cent sodium amalgam and sulphuric acid. The reduction-product was changed into the barium salt, which crystallized in the hard lustrous nodules characteristic of barium sulphoacetate.

The formation of bromsulphoacetic acid by the oxidation of bromoxyethanesulphonic acid proves the correctness of all the formulas used.

### III. (1,2)-DIBROMETHANESULPHONIC ACID.

Bromethylenesulphonic acid and its salts readily combine with hydrobromic acid. 20-gram portions of the potassium salt were heated with fuming hydrobromic acid at  $120^{\circ}$  for five hours. On cooling, a considerable quantity of potassium bromide crystallized out. Enough water to dissolve this was added and the whole transferred to a flask and distilled under 20 mm. pressure until the organic potassium salt began to crystallize out. The rest of the hydrobromic acid was removed

with lead oxide and the liquid evaporated to crystallization. The pure potassium salt of dibromethanesulphonic acid crystallized out in compact, lustrous prisms moderately soluble in cold water, insoluble in alcohol.

I. 0.1716 gram substance gave 0.0497 gram  $K_2SO_4$ .

II. 0.3127 gram substance gave 0.0900 gram  $K_2SO_4$ .

III. 0.1524 gram substance gave 0.1899 gram AgBr.

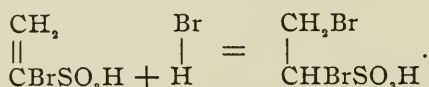
IV. 0.1610 gram substance gave 0.1981 gram AgBr.

V. 0.4841 gram substance gave 0.1331 gram  $CO_2$ , and 0.0479 gram  $H_2O$ .

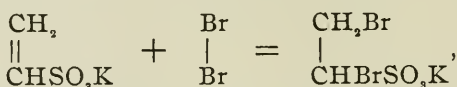
VI. 0.4211 gram substance gave 0.1189 gram  $CO_2$ , and 0.0378 gram  $H_2O$ .

	Calculated for $C_2H_3Br_2O_3SK$ .	I.	II.	Found.		V.	VI.
C	7.84	...	...	III.	IV.	7.5	7.7
H	0.98	...	...	...	...	1.1	1.0
Br	52.28	...	...	52.5	52.7	..	..
K	12.74	12.9	12.9	...	...	..	..

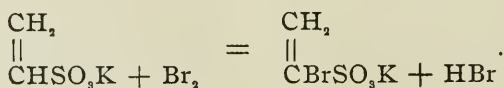
When a solution of this salt is boiled with zinc powder the two bromine atoms are eliminated and ethylenesulphonic acid is formed. The two bromine atoms must therefore be in combination with different carbon atoms and the addition of hydrobromic acid to bromethylenesulphonic acid must take place in the same way as that of water :



The formation of this salt under these conditions is interesting as this is the salt that would be expected to be formed in the reaction between ethylenesulphonic acid and bromine :

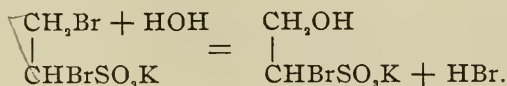


instead of the monobromethylenesulphonic acid always obtained :



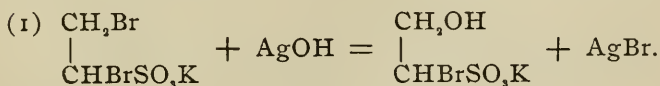


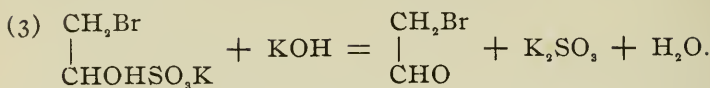
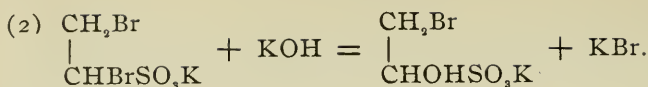
The salt is, moreover, remarkably stable in the presence of water. No hydrobromic acid is given off below the boiling-point of water. Solutions were repeatedly warmed on the water-bath for days without giving a trace of silver bromide with a solution of silver nitrate. On boiling the solution, hydrobromic acid is slowly formed, but the solution contains no unsaturated acid. The hydrobromic acid is due to a reaction with water, resulting in the formation of (1,2)-bromoxyethanesulphonic acid :



In view of these results the experiments with ethylenesulphonic acid and bromine were repeated, fuming hydrobromic acid being used as a medium in place of water. The reaction takes place much more slowly than in water alone, but the product is the same. After removing the hydrobromic acid and evaporating to dryness, the residue was completely soluble in alcohol ; hence, not more than a trace of addition-product can have been formed.

There is an interesting difference in the behavior of the salts of (1,2)-dibromethanesulphonic acid towards those substances which are commonly used for replacing halogen with hydroxyl. It was shown above that when the potassium salt is boiled with water only the bromine atom in the (2)-position is replaced. Potassium carbonate (in dilute solution), potassium acetate, and freshly precipitated silver oxide, react like water. The (2)-bromine atom can be completely replaced with hydroxyl by any of these substances without getting a trace of sulphite into solution. Potassium hydroxide and barium hydroxide attack only the (1)-bromine atom, probably forming a (1)-oxysulphonic acid, which is decomposed as fast as formed, as a molecule of sulphite is formed for every atom of bromine replaced. The difference is illustrated by the following equations :





IV. SULPHONIC ACIDS FORMED BY THE ACTION OF SULPHURIC ACID ON (1)-BROMETHYLENESULPHONIC ACID.

The salts of bromethylenesulphonic acid dissolve in an excess of sulphuric acid forming a number of different sulphonic acids depending upon the conditions.

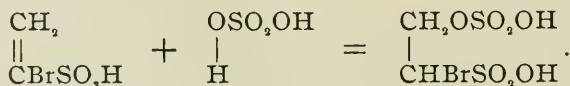
If only a slight excess of sulphuric acid is used, and the temperature kept below  $80^\circ$ , the only product is monobromethionic acid. 20 grams of the barium salt were mixed with an equal weight of sulphuric acid and the temperature kept at  $75^\circ$  for an hour. The liquid was cooled, slowly poured into a liter of ice-water, and neutralized with barium carbonate, ice being added from time to time to keep the liquid at  $0^\circ$ . The neutral liquid was set aside for several days to allow the barium sulphate to settle. The clear solution was then drawn off and concentrated in a vacuum, when a barium salt crystallized out in large colorless plates, mixed with a small quantity of barium carbonate. The salt was redissolved in cold water and concentrated as before. An analysis of the salt, dried on blotting paper, gave the following result :

I. 0.1706 gram salt gave 0.0940 gram  $\text{BaSO}_4$ .

II. 0.2569 gram salt gave 0.1438 gram  $\text{BaSO}_4$ .

	Calculated for $\text{C}_2\text{H}_3\text{O}_6\text{BrO}_2\text{Ba}$ .	I.	Found.	II.
Ba	32.62	32.4		32.8

The salt is readily soluble in cold water. If this solution is boiled barium sulphate is precipitated and (1,2)-bromoxyethanesulphonic acid remains in solution. It is, therefore, the barium salt of bromethionic acid formed by addition of sulphuric acid :



If the barium salt of bromethylenesulphonic acid or the barium salt just described, is mixed with an excess of sul-

phuric acid and the temperature kept at 125° for a few hours an amber-colored liquid is obtained which contains a different sulphonic acid. On neutralizing this liquid as in the preceding experiment, a clear liquid was obtained which became acid on standing. This acidity was not due to sulphuric acid, because no barium sulphate was formed. After neutralizing two or three times in this way and finding the liquid acid after standing for some time, it was finally digested with barium carbonate at 50° until no more barium sulphate was precipitated, then set aside in a vacuum over phosphorus pentoxide. In a short time a very difficultly soluble barium salt separated out in shiny plates, which could not be redissolved without decomposition. An analysis of the hydrous, slightly colored salt gave the following result :

I. 0.6218 gram substance gave 0.0957 gram CO<sub>2</sub>, and 0.0893 gram H<sub>2</sub>O.

II. 0.5880 gram substance gave 0.0884 gram CO<sub>2</sub>, and 0.0687 gram H<sub>2</sub>O.

III. 0.2114 gram substance, oxidized with nitric acid, gave 0.2385 gram BaSO<sub>4</sub>.

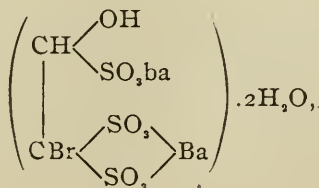
IV. 0.2281 gram substance, oxidized with nitric acid, gave 0.2561 gram BaSO<sub>4</sub>.

V. 0.1620 gram substance, ignited with sulphuric acid, gave 0.0936 gram BaSO<sub>4</sub>.

VI. 0.3104 gram substance, ignited with sulphuric acid, gave 0.1782 gram BaSO<sub>4</sub>.

	Calculated for C <sub>2</sub> H <sub>2</sub> O <sub>10</sub> BrS <sub>3</sub> Ba <sub>1.5</sub> .2H <sub>2</sub> O.	I.	II.	Found. III.	IV.	V.	VI.
C	3.97	4.2	4.1	...	...	...	...
H	0.99	1.5	1.3	...	...	...	...
S	15.74	..	..	15.5	15.4	...	...
Ba	34.05	..	..	...	...	33.8	33.7

The salt was not quite pure but the results agree fairly well with the formula,



which is a bromine substitution-product of a substance obtained by Rathke<sup>1</sup> by the action of acid sulphites on chloral. This formula agrees well with the properties of the salt. When boiled with water, it is decomposed; barium sulphite is precipitated while the solution contains the barium salt of aldehydedisulphonic acid, which separates out on cooling. The salt is difficultly soluble, but can be recrystallized without change. It contains 2 molecules of water of crystallization which are not given off below 100°, where the substance begins to decompose.

I. 0.2613 gram substance gave 0.1332 gram BaSO<sub>4</sub>.

II. 0.2526 gram substance gave 0.1270 gram BaSO<sub>4</sub>.

	Calculated for C <sub>2</sub> H <sub>2</sub> O <sub>7</sub> BrS <sub>2</sub> Ba.2H <sub>2</sub> O.	I.	Found.	II.
Ba	30.17	30.0		29.8

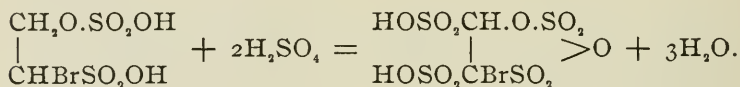
The salt, like those of the unsubstituted acid described by Rathke,<sup>2</sup> is extremely sensitive to alkalis. When warmed with barium hydroxide the aldehyde group is split off as barium formate, which remains in solution while the more difficultly soluble barium salt of brommethanedisulphonic acid separates out from the hot solution in thin plates.

I. 0.2428 gram salt gave 0.1444 gram BaSO<sub>4</sub>.

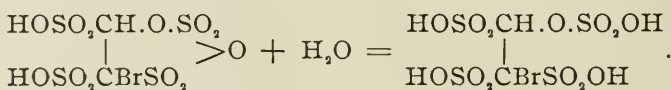
II. 0.2312 gram salt gave 0.1387 gram BaSO<sub>4</sub>.

	Calculated for CHBrS <sub>2</sub> O <sub>6</sub> Ba.	I.	Found.	II.
Ba	35.13	35.0		35.3

These results show that when sulphuric acid reacts with bromethionic acid two hydrogen atoms are replaced by sulphonic acid groups. The primary product seems to be an anhydride:



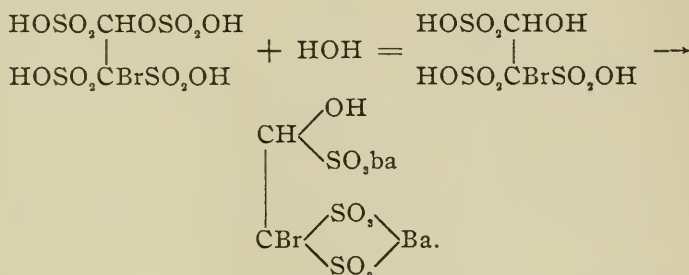
This is slowly decomposed by cold water to form the acid:



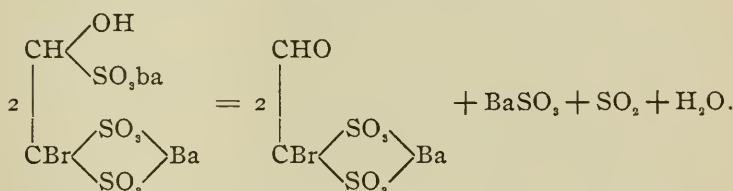
<sup>1</sup> Ann. Chem. (Liebig), 161, 156.

<sup>2</sup> *Ibid.*, 161, 158.

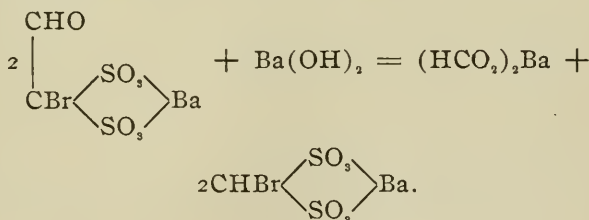
On warming with barium carbonate the sulphuric acid group is split off as sulphate, and the barium salt of bromoxyethane-trisulphonic acid remains :



Like all other (1,1)-oxysulphonic acid salts, this easily loses sulphite and passes into the aldehydesulphonic acid :



The aldehydesulphonic acids are easily decomposed by alkalis. On warming the last salt with barium hydroxide the aldehyde group is split off as formate and the barium salt of brommethanedisulphonic acid is left.



### Summary.

When bromine reacts with ethylenesulphonic acid, dissolved in water, fuming hydrobromic acid, or glacial acetic acid, the first result is the substitution of bromine for the  $\alpha$ -hydrogen atom. This shows a remarkable difference between saturated and unsaturated sulphonic acids. In satura-

ted sulphonic acids it is rarely possible to replace hydrogen with bromine ; in the five unsaturated acids studied, substitution takes place at  $\text{o}^\circ$ .

The (1)-bromethylenesulphonic acid obtained in this way is extremely unstable. There is the same difference between the free acid and the salts, as was observed between polysulphone chlorides and the corresponding acids. When a moderately concentrated solution of the acid is heated to boiling and neutralized with a soluble carbonate from 35 to 50 per cent of it is decomposed—the bromine and sulfoxyl being split off as bromide and sulphite. If an equally strong solution of the potassium salt is boiled with the same carbonate there is rapid addition of water but no elimination of sulphite.

The bromine in bromethylenesulphonic acid behaves like bromine in other unsaturated compounds. Nascent hydrogen replaces it with hydrogen, potassium hydroxide with hydroxyl, and mercuric chloride with chlorine, but it does not lend itself to double decompositions, and it is impossible to link 2 molecules by eliminating halogen by silver.

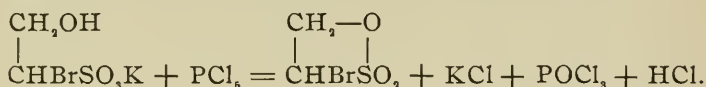
(1)-Bromethylenesulphonic acid differs from the analogous carbonic acids, in that, like ethylenesulphonic acid, it shows no tendency to combine with two atoms of the same kind or with two similar groups. Thus, nascent hydrogen only replaces bromine with hydrogen; and bromine, chlorine, and hypochlorous acid oxidize in the cold. On the other hand, it combines with dissimilar atoms or groups far more readily than most unsaturated carbonic acids. Water, hydrobromic acid, sulphuric acid, acetic acid, and acid sulphites are all slowly taken up in the cold. In all of these cases the negative component of the molecule goes into the (2)-position. The result is a (1,2)-disubstituted ethanesulphonic acid. The (1,2)-oxyethanesulphonic acid obtained in this way is

bromisethionic acid,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHBrSO}_3\text{H} \end{array}$ . A comparison between the

two shows an important difference in the formation of anhydrides and in the behavior towards oxidizing agents. When isethionates are heated they lose a molecule of water for two molecules of salt and pass into diisethionates. The salts of

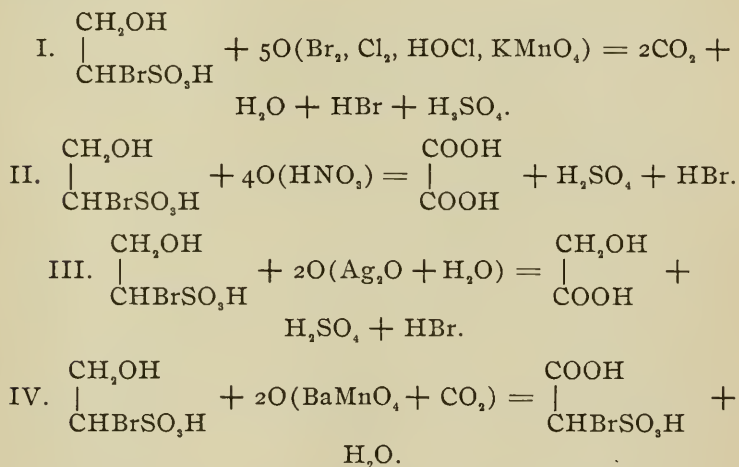


bromisethionic acid behave in the same way, but they are also capable of forming anhydrides from 1 molecule of salt :



No such reaction is possible with isethionic acid. The product is always 2-chlorethanesulphone chlorides.

With potassium permanganate, isethionates always give sulphoacetates which are not affected by an excess of oxidizing agent. The same oxidizing agent completely destroys the bromisethionates even if the liquid is kept neutral with a current of carbon dioxide. The behavior of (1,2)-bromoxyethanesulphonic acid towards different oxidizing agents is interesting :



Two (1,2)-dihalogen ethanesulphonic acids were obtained, one by the action of phosphorus pentachloride on bromoxyethanesulphonic acid ; the other by direct addition of hydrobromic acid to bromethylenesulphonic acid. The salts of these acids are quite stable. By prolonged boiling with water, alkaline carbonates, acetates or silver oxide, the 2-halogen can be completely replaced with hydroxyl, while the (1)-halogen and the sulphonic acid group are left intact. The alkalis and barium hydroxide, on the other hand, instantly

attack the (1)-halogen in the cold, splitting off halogen and the sulphonic acid group, and leaving aldehydes or their polymeric products. With zinc or magnesium both of the halogens can be eliminated with the greatest ease, leaving an unsaturated acid.

CHEMICAL LABORATORY,  
BRYN MAWR COLLEGE.

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## A SERVICEABLE GENERATOR FOR HYDROGEN SULPHIDE.

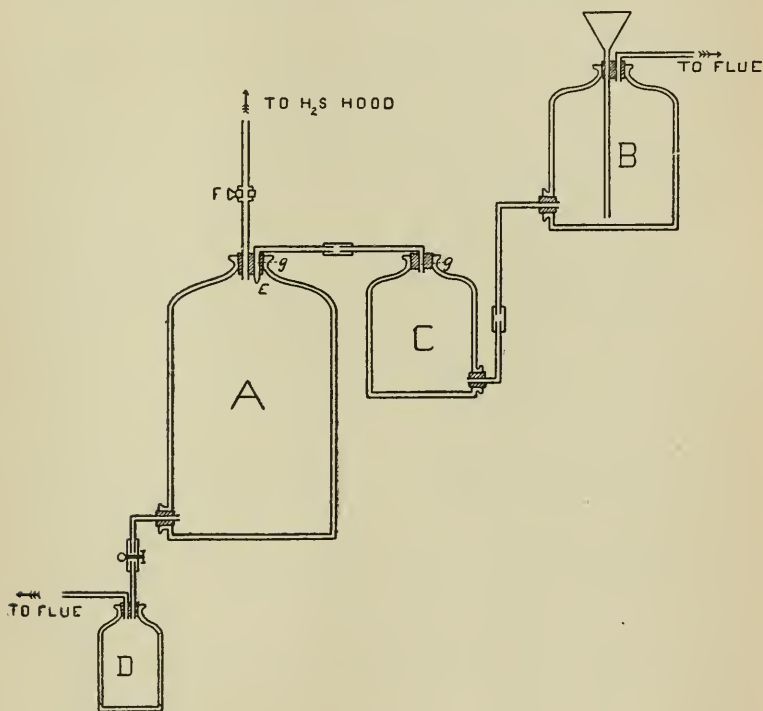
BY W. P. BRADLEY.

The number of gas generators which have been described in chemical periodicals and in part put upon the market is so great that one hesitates before inflicting another upon a long-suffering public. A generator for hydrogen sulphide, however, is subjected by the ordinary class of analytical students to demands so exacting, that probably very few will be found which have met those demands for a period of years with entire satisfaction.

The apparatus to be described has been in use in the laboratory of Wesleyan University in essentially its present form for nine years, and during the latter half of that time has given entire satisfaction both to students and to those who have had the care of it. It consists principally of three glass bottles, *A*, *B*, and *C*, each provided with an orifice near the bottom. *A* is the generator proper, whose mouth is wide so as to admit large lumps of iron sulphide, and whose height is about three times its diameter. It has a capacity of about 16 liters. Through the rubber stopper which closes its mouth passes the gas main, controlled by the main cock *F*, and terminating at a suitable hood in as many distributing cocks as may be desired. Students have access to the distributing cocks only. Through the same stopper enters the acid-supply tube, drawn down at the end *E* to a jet capable of delivering a stream of acid not thicker than the shank of an ordinary pin. This jet projects as little as possible below the stopper. Through the tubulure at the bottom, with its inner end just flush with the stopper, passes a rather thick-walled tube controlled below by a pinch-cock, as shown. By means of this tube the spent

acid is delivered either into a sink or waste-pipe capable of thorough flushing, or into a small bottle, *D*, connected with a flue, which may be detached just below the pinch-cock and emptied as required. The generator bottle is charged with large pieces of iron sulphide until completely full, and *should not be allowed to become less than half full* before recharging. The spent acid must never be allowed to accumulate in such quantities as to reach the top of the sulphide.

*B* is the acid reservoir, wide in proportion to its height,



with a capacity of about 8 liters. The stopper at its mouth admits a funnel whose neck is continued by a glass tube passing to the bottom of the bottle. This reservoir is connected with a flue as shown. The acid used is commercial hydrochloric, diluted with an equal volume of water. A proper charge of acid is the amount necessary to fill *B* half full when

acid is running from, or stands at, the jet *E*. The height at which the reservoir itself is fixed depends, of course, largely on the pressure to be overcome by the gas. A difference of level of 6 inches between the bottom of *B* and the top of *A* has been found ample for ordinary analytical work. If desired, an adjustable support may be used with this reservoir, so that the latter may be raised or lowered at will, and brought down to the level of *A* when the apparatus is not in use. In practice, however, it has been found much better to select once for all such an elevation as will yield somewhat more than the maximum pressure desired.

*C* is the gas reservoir, designed chiefly to retain whatever gas is made after the distributing-cocks, or *F*, are closed. Like *B* it is wide and low. It has a capacity of about 4 liters. Its mouth should be on exactly the same level as that of *A*, and the vertical portions of the tube connecting *C* and *A* are made as short as possible.

The tubing used in the apparatus is, of course, of glass. The rubber stoppers are protected with a thin coating of paraffin, crowded into place while the latter is still warm and soft, and firmly wired. The rubber connections are coated within with paraffin (by pouring hot paraffin through them when perfectly dry), and securely wired.

The working of the apparatus is evident from the foregoing description of its construction. The gas pressure in *A* depends on the difference in level between the top of the acid in *B* and the mouth of the jet *E*. When this pressure is relieved by drawing gas at *F*, a small quantity of acid flows in at the jet and trickles down through the iron sulphide. As soon as the action is fairly established, gas is produced somewhat in excess of the demand, and forcing back the acid, occupies the top of *C*. On the other hand, when the action slackens, the acid flows forward again, driving before it this accumulation. When the demand ceases entirely, gas continues to form slowly for a time, until the last portion of acid admitted is entirely spent. The gas so formed passes into the gas reservoir *C* and fills it from one-third to two-thirds full. Renewed demand for gas is met, of course, at first by this accumulated supply.

Among the special advantages attending the use of this generator may be mentioned economy of acid, uniform efficiency, perfect automatism, and consequently the very slight amount of attention required.

As between the two general types of generator—that in which the acid, after use, is forced back into the reservoir, and that in which the acid never returns, but remains in contact with the iron sulphide—the advantage in point of economy must always lie with the latter. In generators of the former type, either the acid must be discarded before it is completely spent, or else the apparatus begins to work so slowly as to be inefficient. Any one may easily test the matter by throwing a quantity of iron sulphide into a portion of so-called spent acid drawn from an ordinary Kipp apparatus or from any other generator of the former type. Action will take place, somewhat slowly of course, and a quantity of gas, greater or smaller, will be formed. Whatever this amount of gas may prove to be, it represents the loss involved in throwing away the acid in question. And this loss occurs inevitably, whether the spent acid is forced back, as in the Kipp, so as to stand between the fresh acid and the sulphide, or whether, by special arrangements, it is not allowed to return upon the sulphide until all of the acid fresher than itself has been given a chance to act. The amount of this loss may not be worth considering, perhaps, in the case of other gases than hydrogen sulphide, which on the whole are used in much smaller quantity, or even in the case of hydrogen sulphide itself when used for miscellaneous purposes, as in lecture experimentation, etc. But where gas is needed in quantities large in the aggregate, but varying greatly from one time to another, as is the case with hydrogen sulphide required for the work of classes in analysis, the loss from this source in the end is considerable. One who had never tested the matter would doubtless be surprised at the amount of acid thus thrown away. It is scarcely necessary to say that the apparatus now described shares the advantage of economy in this regard with generators of the second type, to which it belongs. Its acid, once admitted to reaction with the iron sulphide, never returns, but continues to act until entirely spent. At the same



time, the efficiency of the apparatus remains entirely constant, because maintained by a flow of uniformly fresh acid.

In being, within the limits of its capacity, entirely automatic, this generator is superior even to others of its own type. Quite universally, in these generators the flow of acid is regulated by a cock introduced somewhere between the reservoir and the generating chamber. This arrangement is sufficiently satisfactory where an unvarying flow of gas is desired or allowable, but requires that the apparatus be placed within easy reach of the operator. It is not advantageous where gas is wanted intermittently and in widely varying quantities, and for student work in analysis is entirely out of the question. With the arrangements here described, the student opens one of the distributing cocks when he wants gas, and turns it off again when he has finished. The flow of acid takes care of itself. The conditions in the hood are exactly the same as if the gas came directly from a gas-holder or storage tank.

To keep the generator in such condition as to meet the demands made upon it in this laboratory by a class of 25-30 students requires a very small amount of care and attention. On the morning of each working day the reservoir is charged with acid (accidents aside it is never found empty), the spent acid is drawn off, and the cock *F* leading into the main is opened, the entire amount of time required of the attendant not exceeding five minutes daily. The iron sulphide bottle is replenished twice a year only.

Finally, the apparatus is so simple that any one can construct it, and once put together it will not get out of order. In its construction tubulated bottles are not at all necessary. Any wide bottles of the proper relative size may be utilized by one who knows how to bore a hole in glass with a broken file.

For some kinds of work uniform gas pressure is required. This is a matter of minor importance in the case of analytical work for which the generator was designed. It is not claimed that this condition is perfectly met, but it can be confidently asserted that with wide, low bottles for *B* and *C*, and with *B* in position at a suitable height above the rest, as given, as uniform a flow of gas is obtained with this generator as with any now on the market, and more so than with most.



One grave objection might be raised to the use of a jet to regulate the flow of acid, namely, that it would be extremely likely to clog by the lodgment in it of solid matter, particularly of sulphur in the case of a generator for hydrogen sulphide. That this objection, which is almost always raised when the present apparatus has been described to those who have never seen it work, is practically of no weight, will appear in the statement that during the entire period of nine years over which the generator has been in use in this laboratory the jet has never clogged.

The dimensions of the various parts of the apparatus as given above are those which have been found on the whole to give the best results for our requirements. Some of them, however, may be varied within certain relative limits. The minimum size of *C* obviously depends on the size of the stream of acid admitted by the jet, for the larger this stream is the more irregular and jerky its flow will be, and the greater the quantity of residual gas to be stored when all the cocks are shut off. On the other hand, no good object could be served by selecting for *C* a bottle of such a volume as would more than accommodate the maximum amount of this residual gas. The acid reservoir *B* should, of course, be at least large enough to hold such a quantity of acid as is needed for the maximum run desired, plus all the acid which may be driven back into it from *C*. The dimensions given contemplate a total available acid charge of 4 liters, or half the volume of the reservoir. As it is highly desirable that the apparatus should not be in need of constant watching, the unoccupied interstitial space between the blocks of iron sulphide in *A* must at all times be as great as the volume of available acid remaining in *B*. If this is not the case, the spent acid may accumulate toward the end of a run so as to stand as high as the iron sulphide, after which, the acid which enters, being specifically lighter, will merely float on top, penetrating to the sulphide by gradual diffusion only, and generating almost no gas. The result of such a condition appears when next the spent acid is drawn off. No sooner does the top layer of unused acid come into contact with the iron sulphide than a quantity of gas is generated which is utterly uncontrollable. This obviously cannot

occur if the generator bottle can accommodate all the available acid of *B* without entirely submerging the iron sulphide. Herein lies the advantage of using the sulphide in as coarse a form as possible, and the reason for giving the generator bottle a capacity not less than twice that of the acid reservoir; *i. e.*, not less than four times the volume of the maximum available acid charge. With such precautions the column of iron sulphide may drop, by use, well down toward half its full height before it can become submerged, with the result that in this laboratory continuous use of the generator for half a year at a time is possible without replenishing the sulphide. Similar considerations indicate the desirability of drawing off the spent acid every time fresh acid is supplied to the reservoir.

It will be seen, therefore, that the actual dimensions stated in describing the apparatus represent a practical minimum with reference to the size of the jet used, and also that any reduction which is attempted in these must be attained by decreasing the size of the latter. How far this may be done without risk of clogging would have to be determined by actual experiment. Whether a small portable generator could be constructed on this principle is, in the judgment of the writer, doubtful. The one described above serves its purpose so well as to leave scarcely anything to be desired.

WESLEYAN UNIVERSITY,  
Jan. 14, 1899.

# AMERICAN CHEMICAL JOURNAL

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Contribution from the Laboratory of General Chemistry, University of Michigan.

## THE ACTION OF METALS ON NITRIC ACID.

### 4. THE REDUCTION OF NITRIC ACID BY SILVER.

BY PAUL C. FREER AND GEORGE O. HIGLEY.

In previous articles<sup>1</sup> an attempt has been made to determine the nature of the action between nitric acid and copper, lead, and silver, with the view of throwing light on the so-called theory of reduction by nascent hydrogen. It was shown that silver and copper have substantially the same action, although copper, with dilute acid, produces some nitrous oxide, which is not formed in the case of silver. On the other hand, with lead the volume of the latter gas is much larger, accounting for from 15 to 70 per cent of the metal dissolved, according to the dilution of the acid. Although, in the case of these three metals, we have considerable variety of action, it was thought best to extend the investigation to a metal still more positive than lead, and therefore iron was finally selected. The metal was in the form of piano wire and was practically chemically pure. Of this 0.2 gram was used in each determination and, as in our previous work, with a large excess of acid. The methods followed were those already described. The results obtained are given in Table I and also in the

<sup>1</sup> This JOURNAL, 15, 71; 17, 18; 18, 587.

TABLE I.  
*Action of Iron on Nitric Acid.*

No.	Sp. gr. acid.	Temp.	Ammo- nia. Mgs.	Equiv. iron.	Nitro- gen. cc.	Equiv. iron.	Nitrous oxide. cc.	Equiv. iron.	Nitric oxide. cc.	Equiv. iron.	Nitrogen dioxide, Mgs.	Equiv. iron.	Iron found.	Iron taken.	Per cent found.
1	10.5	18	11.8	103.7	2.84	18.9	1.84	12.24	22.76	58.5	9.25	3.75	197.2	200	98.6
2	1.05	18	11.9	104.8	2.50	16.7	1.95	13.0	22.1	56.7	2.50	1.00	192.1	200	96.07
3	1.10	18	10.1	88.9	3.56	23.76	2.82	18.77	23.45	60.26	4.9	1.98	193.68	200	96.84
4	1.15	18	7.6	66.7	6.68	44.53	2.73	18.2	25.0	64.2	9.35	3.74	197.54	200	98.77
5	1.20	18	5.3	46.6	5.32	35.40	3.8	25.33	28.63	73.24	17.50	7.01	187.44	200	93.72
6	1.25	18	0.8	7.04	2.73	18.28	2.49	16.56	43.32	111.3	89.24	36.23	189.42	200	94.71
7	1.30	18					2.29	15.24	42.5	109.2	186.8	75.84	200.28	200	100.14
8	1.35	18							39.3	101.0	234.8	95.32	196.32	200	98.16
19	1.40	70							30.8	79.15	282.9	114.9	194.4	200	97.2
10	1.40	70							32.8	83.0	265.9	107.9	190.9	200	95.45
11	1.40	70							8.7	16.6	427.8	173.6	190.2	200	95.1

curves in Plates I and II, with specific gravity of acid as abscissae and per cent of metal equivalent as ordinates.

*Discussion of Data.*

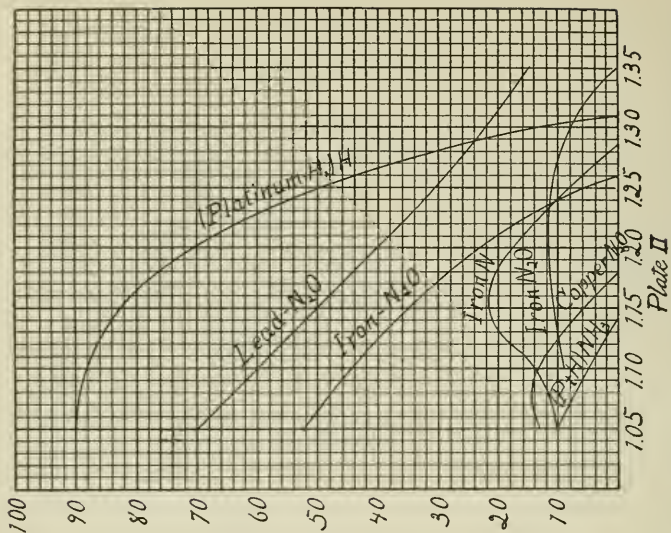
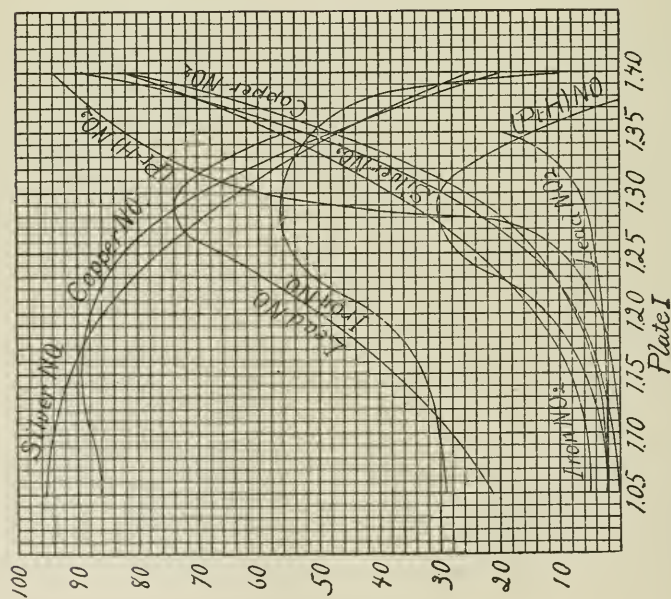
The reduction products are nitrogen dioxide, nitric oxide, nitrous oxide, nitrogen, and ammonia. When iron is dissolved in nitric acid (sp. gr. 1.40) nitrogen dioxide and nitric oxide are obtained in proportions differing considerably with varying amounts of solvent. Thus in Experiments 9 and 10, in which 7 cc. of acid were introduced, there were 40 per cent of nitric oxide to 60 per cent of the dioxide, while in No. 11, with 10 cc. of acid, the ratio was 10 to 90. These differences, due to the change in the mass of acid, confirm our view, which will be developed below, that nitric oxide, in the action of metals on nitric acid, is solely a secondary product of the decomposition of the dioxide.

As the acid diminishes in strength the variation in the relative amounts of these two products is much like that observed with other metals until a specific gravity of 1.30 is reached, when nitrous oxide is formed in amount equivalent to about 8 per cent of metal dissolved; with acid having a sp. gr. of 1.25 the reaction is further complicated by the appearance of nitrogen and ammonia, the former reaching a maximum at 1.15, and then falling, while the latter (the most important product of the reduction of dilute nitric acid by iron) rises to a maximum at 1.05. The amount of ammonia obtained from acid having a specific gravity of 1.25 is 0.0008 gram, equivalent to 7.04 per cent of the metal dissolved; with acid of specific gravity 1.05 the equivalent is 52 per cent.

These results are not in harmony with those obtained by Acworth and Armstrong,<sup>1</sup> who investigated the action of iron on nitric acid of specific gravity 1.20 to 1.03, approximately. These chemists report only three reduction-products, nitric oxide, nitrous oxide, and nitrogen, in proportions not differing very widely from those obtained by us with the same strength of acid, but their percentage of metal accounted for was low, varying from 64.23 per cent with 1.20 to 44.44 per cent with 1.03 acid. This deficiency of metal is accounted for, 1st, by

<sup>1</sup> J. Chem. Soc., 32, 79.





NOTE.—In Plate II, in the upper of the two curves marked "Iron— $N_2O$ ," for "Iron— $N_2O$ ," read "Iron— $NH_3$ ."



the fact that nitrogen dioxide was absorbed in the potash bulb which was interposed between the generator and the pump ; and 2nd, by the fact that the considerable quantities of ammonia produced from all acid of the above concentrations were overlooked. Take, for example, their result with 1 : 8 acid. If to their per cent of metal (44.44) there be added our metal equivalent of nitrogen dioxide and ammonia (1 plus 52) the sum is 98.4 per cent. A similar, though smaller, correction might be made throughout their whole work with iron.

Silver, copper, and iron have thus a similar action on concentrated nitric acid (1.40 to 1.35), the products being solely nitrogen dioxide and nitric oxide, although in somewhat different proportions ; indeed, the curves with silver and copper are throughout nearly identical. The specific action does not become strongly marked until a greater dilution (*i. e.*, greater ionization) is reached. It is evident that the non-ionized acid acts simply as an oxidizer, giving off the least possible quantity of oxygen to form the dioxide, nitric oxide appearing as a secondary product only, in consequence of the action of water on the dioxide. This view is confirmed by the fact cited above, that the relative amounts of these two reduction-products can be varied by changing the mass of the acid. Silver and copper also have substantially the same action on nitric acid of medium strength (1.20) giving 10 per cent nitrogen dioxide and 90 per cent nitric oxide. Lead with the same dilution, however, yields nitrous oxide equivalent to about 40 per cent of metal, nitric oxide equivalent to 50 per cent, and dioxide only in the proportion of about 2.5 per cent. It will be observed that the nitrous oxide curve for lead rapidly rises as that for the dioxide falls, but that its nitric oxide curve, at a dilution of 1.27, is as yet at the same point as this product is with silver and copper. This fact strengthens our view that the oxides below nitric oxide are due to a reduction of nitrogen dioxide and not of nitric acid, but that nitric oxide itself is a result of aqueous decomposition. Iron reduces acid of specific gravity 1.20 more completely, as nitrogen and ammonia, equivalent respectively to 17 and 23 per cent, are given off. Finally, with acid of specific gravity 1.05, the differences in the results obtained with the four metals are very considera-

ble. Nitrous oxide is now found in small quantities among the products obtained with copper, but there is none with silver (see Plate II) ; lead produces nitrous oxide equivalent to about 70 per cent of metal dissolved, and iron yields this substance only in small amount (6 per cent). The latter metal is also quite different from lead as well as from silver in that it yields nitrogen and ammonia equivalent to 8 and 52 per cent of metal. Each metal, therefore, has its own specific action on dilute nitric acid, and, in respect to the degree of reduction, they must be arranged in the following order, beginning with the weakest: silver, copper, lead, and iron. If, however, the concentration of the acid is somewhat greater (1.35), then lead acts more energetically than iron.<sup>1</sup> The metals which produce no oxides below nitric oxide (or at least, as with copper, very little nitrous oxide) have very nearly identical curves for the reduction products which are formed.

*The Mode of Action between Metals and Nitric Acid.*

It has already been pointed out in discussing the mode of action of acid between metals and strong nitric acid that the changes are, in all probability, due to direct deoxidation. With more dilute acid, which is ionized to a greater degree, there may be two theories :

1. The metallic atom takes up a positive charge from a hydrogen ion of the metallic salt, while the hydrogen, losing its charge, becomes nascent and effects reduction in different degrees, according to the metal at whose surface it is liberated, and thus becomes capable of either attacking the  $\text{NO}_3$  ions of a second molecule or, as seems more probable, of reducing the nitrogen dioxide which has been formed. This may seem but another way of stating the theory of nascent hydrogen in its older form, but that in reality it embodies a notable difference will appear from the work on the electrolysis of nitric acid which follows. The character of the reduction-products and their relative quantities thus depends upon the degree of ioni-

<sup>1</sup> In discussing the action of lead on concentrated nitric acid it must be borne in mind that the metal does not act on acid of a greater concentration than 1.35. Were it to act on the other strengths it is evident from the curve that nearly the same percentage of dioxide would be produced as is obtained with copper and silver.

zation of the acid and also upon the energizing effect of the metal, upon the surface of which the action takes place, the variations being due to the more or less positive nature of the latter.

2. The metallic atoms, acting in conjunction with the hydrogen of a molecule of nitric acid, attack and deoxidize a  $\text{NO}_2$  group (or nitrogen dioxide), thus forming water and metallic oxide, the latter neutralizing the acid to produce a nitrate. This second view also contains something of the nascent hydrogen theory. The above considerations made it probable that the effect of electrolytic hydrogen compared with that of copper, silver, lead, and iron acting on the same strength of acid might give results which would go far toward settling the question as to which of these two modes of action is the more probable. If the first is correct, *i. e.*, if hydrogen alone, occluded and energized by the undissolved metal, is the reducing agent with dilute acid, then an electrolysis of the same acid in cells provided with anodes of platinum and with kathodes of silver, copper, and lead, respectively, should at the latter poles yield products differing qualitatively and quantitatively somewhat as do those obtained by the solution of the same metals without the electric current, the acid being of the same specific gravity. For example, lead has been shown to be a much more energetic reducing agent than silver. Suppose two cells, filled with nitric acid of specific gravity 1.05, to be provided with anodes of platinum and kathodes of silver and lead having equal area; if now, on passing a current through these cells in series, the reduction-products are found to be substantially the same, both qualitatively and quantitatively, then, since the action of metal ions is excluded and the reduction is effected by hydrogen ions in contact with the respective metals, the proof would be fairly satisfactory that the wide differences observed in the results of the solution of silver and lead in nitric acid of specific gravity 1.05, are not due to the action of nascent hydrogen. On the other hand, if the products in these two cells should differ widely, those at the lead kathode containing relatively less oxygen than those found at the one formed of silver, this

would indicate the participation of metal atoms in the reduction of nitric acid.

It was therefore decided: 1st, to investigate the action of electrolytic hydrogen upon all the strengths of nitric acid which had been employed in the preceding work, and 2nd, to determine the relative action upon acid of specific gravity 1.05 of electrolytic hydrogen, liberated at kathodes of platinum, silver, copper, and lead.

#### 5. THE ELECTROLYSIS OF NITRIC ACID.

This is not an untrodden field. Faraday<sup>1</sup> has shown that when strong nitric acid is electrolyzed, no hydrogen appears at the kathode, but that, on the other hand, a yellow or reddish color, probably due to nitrous acid, is seen. A different result was, however, obtained on mixing the acid with an equal or greater volume of water, for then hydrogen was produced, the amount of the gas depending both upon the concentration of acid and upon the current employed. To use Faraday's own words, "that acid from which no gas separated at the kathode with a weak voltaic battery, did evolve gas there with a stronger; and that battery which evolved no gas there with a strong acid, did cause its evolution with an acid more dilute."

A little later Schönbein<sup>2</sup> made a series of determinations of the action of electrolytic hydrogen on nitric acid ranging from 1.49 to 1.07 in specific gravity, his object being to determine the conditions under which there is complete oxidation of the hydrogen. Bourgoin<sup>3</sup> subsequently confirmed Faraday's results with concentrated acid, but found that when dilute nitric acid is electrolyzed, some nitrogen and nitric oxide, as well as considerable quantities of ammonia, are produced. Gladstone and Tribe<sup>4</sup> also electrolyzed acid of specific gravities 1.40, 1.20, and 1.13, respectively, employing various current densities. These investigators found that from the first concentration, neither ammonia nor hydrogen was obtained with

<sup>1</sup> Phil. Trans., 1834, 96.

<sup>2</sup> Pogg. Ann., 47, 563.

<sup>3</sup> Jour. Pharm. (4), 13, 266.

<sup>4</sup> J. Chem. Soc., 35, 172.

any current employed ; with the second neither of the above compounds was evolved when a current from a single Grove cell was used, but with increased current density hydrogen was obtained. The third gave a reduction of about 50 per cent of the theoretical at the kathode, when two cells were used, but this number fell to less than 1 per cent when eight cells were employed, the hydrogen in this last case being about 98 per cent of that required by theory. No ammonia was detected.

Subsequently Ihle investigated<sup>1</sup> the conditions favorable to the formation of ammonia during the electrolysis of nitric acid. By greatly varying the area of the platinum kathode, he found that an increase in the current density caused an increase in the ammonia formed, but that with given current density the amount of this substance diminished with increasing concentration of acid.

#### *Experimental Part.*

The apparatus employed consisted of a large U-tube provided with electrodes of platinum wire  $\frac{1}{4}$  mm. in diameter, fused into the glass and bent into a flat spiral. The kathode was 65 mm. in length, and had therefore an area of about 50 square mm. A few centimeters below the kathode a narrow glass tube was sealed into the U-tube, and through this a current of carbon dioxide was admitted. The reduction-products and the hydrogen were passed through concentrated sulphuric acid, and all gas that remained unabsorbed was collected in a Schiff azotometer over caustic potash (1 : 1). The necessary connections of the apparatus were of ground glass. The gases were analyzed in all respects as described in the previous papers ; the relative amounts of nitric oxide and dioxide absorbed by the sulphuric acid being determined by titration with permanganate, and the total nitrogen as nitric oxide by means of the nitrometer. Hydrogen was found by explosion with an excess of oxygen, and ammonia by titration with standard acid. The results of the work are shown on Plates I and II and in Table II.

<sup>1</sup> Ztschr. physik. Chem., 19, 572.

TABLE II.

No.	Sp. gr. acid.	Current.	Voltammeter. Hydrogen. cc.	Hydrogen.	Per cent.	Ammonia. Mgs.	Per cent.	Nitric oxide. Mgs.	Per cent.	Nitrogen dioxide. Mgs.	Per cent.
1	1.40	0.100	20.8							81.3	93.3
2	1.40	0.100	34.8							82.8 <sup>1</sup>	
3	1.35	0.100								109.5 <sup>1</sup>	
3 <sup>1</sup>	1.35	0.010								26.5 <sup>1</sup>	
4	1.35	0.100									
5	1.30	0.100		3.0	9.9			4.79	13.8	135.4	86.2
6	1.25	0.100	34.8	17.9	51.4			8.6	30.8	75.9	59.3
7	1.20	0.100	31.3	24.7	78.9			8.47	26.7	12.63	8.9
8	1.15	0.100	48.7	36.0	73.9			2.5	8.8	3.81	2.9
9	1.10	0.100	25.6	21.46	83.8	0.1	2.03	2.9	6.6	3.88	2.2
10	1.05	0.100	31.32	25.28	80.7	0.6	10.0				
11	1.05	0.100	42.6	35.7	83.8	0.3	5.5				

<sup>1</sup> Cell not heated to expel all products. During the electrolysis the cell was kept at the temperature of the room.



The reduction-product obtained from acid of specific gravity 1.40 was pure nitrogen dioxide.<sup>1</sup> This was the case both when the cell was heated, after the current had been turned off, to expel all the gaseous products (Experiment 1), and also when an analysis was made of those gases only which were swept forward by carbon dioxide at the temperature of the room (Experiments 2, 3, and 3'). With acid of specific gravity 1.35, attempts were made to determine the effects of widely different current densities (Experiments 3 and 3'). The results were the same—nitrogen dioxide was the sole product. In Experiment 4, however, with the same strength of acid, nitric oxide was obtained in quantity equivalent to about 14 per cent of the total product. This was the most dilute acid which yielded no hydrogen, for when that of specific gravity 1.30 was employed, this gas was freely evolved for some minutes, at the kathode, and then suddenly ceased.<sup>2</sup> The remaining products were nitric oxide and dioxide amounting to 30.8 per cent and 59.3 per cent, respectively, of the total. Acid of specific gravity 1.25 yields a much larger percentage of hydrogen (51.4 per cent), nitric oxide being somewhat, and nitrogen dioxide greatly, diminished; with greater dilution, the amount of both of the latter substances is much less, and they practically disappear when the specific gravity is 1.10. Ammonia was obtained in small amounts with acids of the specific gravities 1.05 and 1.10.

Electrolytic hydrogen then, acts upon concentrated nitric acid much the same as do silver, copper and iron, nitrogen dioxide being the principal product in each case, a fact that supports the view expressed above, that the action consists in direct deoxidation; with acid of medium concentration, however, it behaves (at least with the current density employed by us) quite differently from the metals mentioned, since a large percentage (75 per cent) escapes oxidation. Finally, electrolytic hydrogen in its action upon dilute acid, resembles iron more than any of the other metals with which we have

<sup>1</sup> The fact that the dioxide was not decomposed in these cases is undoubtedly due to the very large excess (20 cc.) of nitric acid present. Had an equal amount of this strength of acid been employed in the parallel experiments with the metals, pure dioxide would undoubtedly have been obtained in each case.

<sup>2</sup> This cessation of the evolution of hydrogen is attributed by Gladstone and Tribe to the action of nitrous acid (*loc. cit.*, 174).

experimented, since a considerable amount of ammonia is produced.

6. COMPARISON OF THE ACTION OF ELECTROLYTIC HYDROGEN LIBERATED AT KATHODES OF PLATINUM, SILVER, LEAD, AND COPPER.

Some preliminary experiments were made in which ammonia was the only product determined. The apparatus employed in this part of the work consisted of four cells made of small beakers, each provided with a diaphragm of unglazed porcelain, with anodes of platinum, and kathodes of platinum, silver, lead, and copper foil, respectively; each electrode had an area of 100 square mm. The cells were filled with nitric acid having a specific gravity of 1.05, and were connected in series with a battery, a millammeter, a voltammeter and suitable resistance. The current employed varied from 0.2 to 0.5 amperes. It was found that the evolution of gas at the electrode of copper was but slight, even when a current of 0.5 amperes was employed, but that given off at the kathodes of lead and of silver was considerably greater.

The results are shown in Table III, in which are given

TABLE III.

No.	Current density : amperes per sq. mm.	Ammonia—milligrams.								
		Calculated from voltammeter.	Found at kathode of							
			Copper.	Per cent.	Lead.	Per cent.	Silver.	Per cent.	Platinum.	Per cent.
1	0.002	9.04	7.9	87.4	2.7	29.8	2.7	29.8	0.2	2.2
2	0.005	20.8	16.8	80.8	8.7	41.3	5.1	25.5	0.66	3.2

current density in amperes per square millimeter, theoretical ammonia as calculated from voltammeter results, and ammonia as produced at the kathodes of copper, lead, silver, and platinum, with the respective percentages. At the close of one experiment it was found that the platinum kathode was nearly covered with a thin coating of copper, from the accidental contamination of the cell contents with a small amount of copper salt. An analysis of the liquid in this cell showed ammonia to the amount of 65.5 per cent of the theoretical.

Having shown that the production of ammonia is an important result of the electrolysis of dilute nitric acid, whether

copper, silver, or lead is employed as kathode, it seemed desirable to determine the other reduction-products. A series of experiments was therefore made in a modified apparatus, similar to that described above, except as noted later. The kathode had an area of 100 square mm. The results are given in Table IV. As will be seen, the sole products obtained from the reduction of nitric acid of specific gravity 1.05, by electrolytic hydrogen at the surface of kathodes of copper, silver, and lead are nitrogen and ammonia.

The effect of high current density is apparent both in the work with copper and silver. Thus in Experiments 1 and 2, in which a current density of 0.001 was employed, the per cent of ammonia varies from 81.1 to 88.6, while in Experiments 3 and 4, in which the kathode was a wire about 20 mm. in length and 0.5 mm. in diameter, placed parallel to the direction of the current, no nitrogen was collected, and ammonia was recovered, equivalent to 96 to 100 per cent of the theoretical. In the work with silver, similar results were obtained. Experiments 7, 8, and 9 demonstrate this fact, the current density in these cases being comparatively low (0.002 to 0.005) and the result a high percentage of nitrogen (63 to 66) and low ammonia (22 to 27.4). In Experiment 10, in which the kathode was a wire about 20 mm. in length and 0.25 mm. in diameter, placed as described above, the percentage of ammonia rose to 54.5, and that of nitrogen fell to 37.6. These results are in harmony with those of Ihle<sup>1</sup> who used kathodes of platinum.

#### *Conclusions.*

1. Silver, copper, iron, and electrolytic hydrogen have nearly the same effect on concentrated nitric acid, nearly pure nitrogen dioxide being evolved.

2. In respect to their action on dilute nitric acid, the order of the metals silver, copper, lead, and iron is that of the potential series.

3. The activity of electrolytic hydrogen depends, in a marked degree, upon the character of the electrode upon whose surface it is liberated.<sup>2</sup>

<sup>1</sup> *Loc. cit.*, 574.

<sup>2</sup> Traube has shown that electrolytic hydrogen acts upon oxygen molecules to produce peroxide at the surface of platinum electrodes, but not at electrodes of carbon.

TABLE IV.

No.	Current.	Current density in amperes per sq. mm.	Voltammeter cc. of oxygen.	Nitrogen, cc.	Per cent.	Ammonia, Mgs.	Per cent.	Total per cent.	Kathode.
1	0.1	0.001	73.42	1.44	18.3	7.6	81.1	99.4	Copper
2	0.1	0.001	80.47	1.11	10.1	9.1	88.6	98.8	"
3	0.1	1	millammeter	0	0	15.4	96.4	96.4	"
4	0.03	1	Two hours millammeter	0	0	2.6	100.0	100.0	"
5	0.2	0.002	One hour 166.9	13.8	61.9	6.1	28.7	90.7	Lead
6	0.2	0.002	162.9	15.9	73.3	5.4	25.9	99.2	"
7	0.5	0.005	150.6	12.6	62.8	4.60	23.9	86.7	Silver
8	0.5	0.005	143.8	13.0	67.4	4.01	22.0	89.4	"
9	0.2	0.002	154.5	13.2	65.0	5.4	27.4	92.4	"
10	0.1	1	Two and one-sixth hours millammeter	10.3	37.6	9.45 <sup>2</sup>	54.5	92.1	"

<sup>1</sup> Wire kathode employed. Current density very high.<sup>2</sup> Kathode blackened.

4. Electrolytic hydrogen, in contact with kathodes of copper and of silver, effects reduction of nitric acid in proportion to the current density. (Data are wanting in regard to lead.)

5. When nitric acid having a specific gravity of 1.05 is subjected to electrolysis in cells having kathodes of silver and lead, respectively, on the surface of which kathodes there is equal current density, the reduction products are the same; *i. e.*, nitrogen and ammonia, in approximately the same proportions.

6. Silver and lead, when dissolved in acid of specific gravity 1.05, yield reduction products which are widely different, both qualitatively and quantitatively, since from the silver there is obtained only nitric oxide and nitrogen dioxide equivalent respectively to 95 per cent and 5 per cent of metal dissolved, while with lead the products are nitric oxide, nitrogen dioxide, and nitrous oxide, equivalent in the order named, to 2.5, 7.5, and 70 per cent of metal dissolved.

7. Lead reduces nitric acid of specific gravity 1.05 much more completely than copper, yielding about five times more nitrous oxide than the latter. On the other hand, copper, when made the kathode of an electrolytic cell containing the same strength of acid, has a much greater energizing effect upon the hydrogen deposited upon its surface than is shown by lead under the same circumstances, and produces about three times as much ammonia as the latter. This conclusion is even more emphatically impressed on us by comparison of the results with lead and silver.<sup>1</sup>

8. Since, in the electrolysis of nitric acid with a constant current, the action of metallic ions is excluded, and the reduction must be effected by the hydrogen ions in contact with the surface of the different metals, and since, therefore, the hydrogen ion, in contact with the respective metals, is the sole reducing agent, it follows that the widely different products obtained when lead and silver dissolve in nitric acid cannot be attributed to the action of the hydrogen atoms alone, but must also involve the direct deoxidizing effect of the metals themselves. Undoubtedly with the concentrated, and

<sup>1</sup> It must be borne in mind that the kathodes do not change in weight during electrolysis.

hence not ionized, acid, the metals alone cause the change, but with a greater dilution both metals and hydrogen unite in causing reduction. The theory of nascent hydrogen cannot therefore be held in regard to the stronger acids, in which only nitrogen dioxide and nitric oxide are given off, but, subject to the modifications given above, is undoubtedly valid in relation to dilute acid.

We take this opportunity of thanking Dr. Karl E. Guthe, of the physical laboratory, for his helpful suggestions.

ANN ARBOR, January, 1899.

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## ON THE DISSOCIATION OF PHOSPHORUS PENTABROMIDE IN SOLUTION IN ORGANIC SOLVENTS.

BY J. H. KASTLE AND W. A. BEATTY.

In connection with other investigations which have been conducted in the laboratory of the State College of Kentucky during recent years, we have often observed that many bromine compounds of the most diverse types possess at least one property in common; *viz.*, that they are yellow in the solid state and dissolve in inert organic solvents, such as chloroform, ether, carbon bisulphide, and the like, with the production of a reddish-yellow solution, which in tint closely resembles a solution of bromine itself. The idea, therefore, suggested itself that in such solutions bromine compounds are either wholly or partly dissociated, or perhaps in many instances decomposed in such a way that bromine itself is set free in the solution, thereby imparting the orange-red color which is characteristic of so many bromine compounds. Among the less complicated bromine compounds exhibiting such properties is phosphorus pentabromide. This can be obtained without difficulty in a state of purity, and in the form of beautiful, yellow, rhombic prisms. When heated in a sealed tube it melts to a dark red liquid, which on being further heated is converted into vapor and dissociated, giving dark red vapors of bromine. As the products of the dissociation pass to the colder parts of the tube they recombine and the original substance is deposited in beautiful crystalline



condition. Phosphorus pentabromide is also readily soluble in carbon bisulphide, chloroform, carbon tetrachloride, etc., with the production of red solutions. This compound was, therefore, selected as probably a good substance with which to begin an inquiry into the causes of such phenomena as those under discussion. A quantity of phosphorus pentabromide was prepared by bringing together phosphorus tribromide and bromine in theoretical proportions by weight. The resulting product was found to consist of both the yellow and the red varieties of the compound, the former largely predominating in amount. It was then purified by sublimation in sealed tubes at the temperature of the water-bath, as the result of which it was obtained in the form of large, well-defined, transparent, yellow crystals. Smaller needle-shaped crystals of the red variety were also often obtained by this method of purification, but only in small amounts. The two varieties were, however, usually found to occupy different positions in the tube, and were never so intimately mixed that they could not be readily separated in transferring to the weighing-bottle. At the completion of the sublimation the sealed tubes were opened, and the best crystals of the yellow variety were transferred as rapidly as possible to a weighing-bottle. In consequence of the great affinity of this compound for atmospheric moisture it was not attempted to preserve it for any length of time, but it was used immediately in the preparation of standard solutions in the solvent under investigation. Further, the standard solutions of the phosphorus pentabromide were not kept longer than one day for fear of alteration by the action of the moisture of the air, so that the effect of long standing on the character of such solutions has as yet not been determined.

Carbon bisulphide was the first solvent investigated. In this solvent phosphorus pentabromide dissolves with great ease to form a dark red solution, which on evaporation in the cold deposits both the red and yellow varieties of the pentabromide. This dark-red solution in carbon bisulphide was found to have exactly the same color as solutions of free bromine in the same solvent; and hence the attempt has been made to measure the extent of the dissociation of phosphorus penta-

bromide in carbon bisulphide by comparing such solutions colorimetrically with solutions of bromine in the same solvent—the strength of the latter being determined by means of decinormal solutions of iodine and sodium thiosulphate. The color comparisons were made in flat-bottomed glass cylinders of exactly the same bore, and having very thin walls. The volumes of the solutions of the pentabromide and the standard solutions of bromine with which it was compared were always made the same for each comparison, so that the depth of color was always measured on the same bulk of solution. The colorimetric method as applied here is by no means free from objections, but for certain dilutions, varying from 1/100 to 1/500 N, it leaves little to be desired in point of accuracy. With more concentrated solutions, however, for example 1/10 N, the depth and intensity of the color was found to be such as to prevent exact comparison with the standard solutions of bromine, by means of the appliances now at our disposal, and hence no measurements at a concentration greater than 1/100 N have as yet been made, and at dilutions greater than 1/1000 N no very exact measurements could be made on 10 cc. portions, on account of the extreme lightness of the tints; and hence no comparisons have been attempted at dilutions greater than 1/1000 N. In fact, as will be seen, from the results obtained at greater concentrations, there does not seem to be any necessity for making these measurements on extremely dilute solutions, inasmuch as the pentabromide seems to be completely dissociated even at much greater concentrations. It is highly important, however, to make these color comparisons at dilutions greater than 1/1000 N, and for this purpose we hope shortly to devise a satisfactory method. The following results have been obtained for the dilutions indicated.

*Table I.*

Dilution of $\text{PBr}_5$ in carbon bisulphide.	Cc. $\text{PBr}_5$ solution used in each experiment.	Cc. bromine solution required to give the same color as $\text{PBr}_5$ .
1/100 N	10	0.5 Sol. I
1/100 N	10	0.9 Sol. II
1/100 N	10	0.9 Sol. II
1/200 N	10	0.85 Sol. III
1/200 N	10	0.9 Sol. III
1/500 N	10	1.7 Sol. IV
1/1000 N	10	0.9 Sol. IV

Quantity of bromine required to give the color of the $\text{PBr}_5$ solution. Gram.	Theoretical quantities of bromine set free in dissociation of $\text{PBr}_5$ .	Percentage dissociation.
0.0177	0.0160	110.6
0.0161	0.160	100.6
0.0161	0.160	100.6
0.0075	0.080	93.8
0.0079	0.080	98.8
0.0031	0.0032	96.9
0.0016	0.0016	100.0

*Strength Br Solutions Used in Above Table.*

Bromine, Solution I	contained	0.0354882	gram Br per cc.
" " II	"	0.0178915	" " " "
" " III	"	0.0087696	" " " "
" " IV	"	0.0018009	" " " "

These results certainly seem to indicate that phosphorus pentabromide is completely dissociated in carbon bisulphide solution, according to the equation :



at all dilutions ranging from 1/100 to 1/1000 N, and the view that the change in question is really one of dissociation, and not a non-reversible decomposition, into phosphorus tribromide and bromine finds support in the facts that both the red and yellow crystalline modifications of the pentabromide can be obtained from its solutions in carbon bisulphide. The conduct of pentabromide towards heat in a closed tube, and also the conduct of phosphorus pentachloride in the gaseous state might also be cited in support of this conclusion. And in this connection it should be observed that the formation of such red solutions by phosphorus pentabromide, which itself is yellow, would be extremely difficult of explanation upon any other grounds than those involving the dissociation of the compound into the tribromide and bromine, this latter imparting the characteristic red color to such solutions. The color of phosphorus pentabromide in the solid state at ordinary temperatures is not very different from that of octahedral sulphur. Solutions of sulphur in such solvents as carbon bisulphide, naphthalene, etc., have a yellow color, whereas, as

has been repeatedly stated, similar solutions of phosphorus pentabromide have the red color of bromine. In solutions of sulphur the characteristic yellow color is imparted by molecules of sulphur, whereas the supposition seems justified that in solutions of phosphorus pentabromide the characteristic red color is imparted by molecules of bromine—this latter substance having resulted from the dissociation of molecules of the pentabromide.

It has also been observed in this connection that the addition of phosphorus tribromide to the solutions of the pentabromide in carbon bisulphide causes them to become lighter in color, and conversely solutions of phosphorus pentabromide in the tribromide become darker in color on the addition of carbon bisulphide. This, of course, signifies that the phosphorus tribromide as one of the products of the dissociation exerts a repressive effect on the change in question, and by its presence drives a certain amount of the product of the dissociation into combination, and, as is well known, such phenomena are characteristic of the dissociation process.

Similar experiments have been tried using carbon tetrachloride as the solvent. In this solvent phosphorus pentabromide dissolves to form a red solution, which in tint is exactly comparable with a solution of bromine in this solvent. The results obtained with carbon tetrachloride are given in full in Table II.

Table II.

Dilution of $\text{PBr}_5$ in carbon tetrachloride.	Cc. $\text{PBr}_5$ solution used in each experiment.	Cc. bromine solution required to give the color of the $\text{PBr}_5$ solution.
0.5157 gram $\text{PBr}_5$ in 50 cc. $\text{CCl}_4$ .	5	2.8
0.5157 gram $\text{PBr}_5$ in 100 cc. $\text{CCl}_4$	10	2.8
0.3093 gram $\text{PBr}_5$ in 100 cc. $\text{CCl}_4$	10	1.6
0.2062 gram $\text{PBr}_5$ in 100 cc. $\text{CCl}_4$	10	1.1
0.1031 gram $\text{PBr}_5$ in 100 cc. $\text{CCl}_4$	10	0.5

Quantity of bromine required to give the color of the $\text{PBr}_5$ solution. Gram.	Theoretical quantities of bromine set free in complete dissociation of $\text{PBr}_5$ .	Percentage dissociation.
0.0175	0.01914	91.4
0.0175	0.01914	91.4
0.0100	0.0115	87.0
0.0069	0.0077	89.6
0.0031	0.0038	81.6

The solution of bromine in carbon tetrachloride used in these measurements contained 0.006264 Br per cc.

It will be seen from these results that in solutions of carbon tetrachloride, as dilutions varying from about  $1/40$  to about  $1/400$  N, phosphorus pentabromide is dissociated to the extent of 90 per cent. This would seem further to represent the maximum dissociation of this compound in this solvent inasmuch as no increase in the dissociation was observable in passing from the lowest to the greatest of these dilutions. In fact, as will be seen in the above table, there seems to be a falling off in the dissociation from 91.4 to 81.6 per cent in passing from  $1/40$  to  $1/400$  N dilution. This is believed, however, to be due to an error in the colorimetric determination at the greater dilution—the very light tint obtained at this great dilution with this solvent rendering exact comparisons with the standard bromine solution difficult and uncertain. Further, any slight error with such small amounts as are present at this dilution would be considerably magnified in the calculation of results. The fact that the dissociation of phosphorus pentabromide in carbon tetrachloride is less by 10 per cent than in carbon bisulphide, in which latter solvent it was found to be complete, is rather remarkable, and at present no sufficient reason for this has been found. It should be noted in this connection, however, that the solubility of phosphorus pentabromide is considerably less in carbon tetrachloride than in carbon bisulphide. In the former solvent it was found to dissolve only sparingly, whereas in the latter it was very freely soluble. It may be that this difference in solubility will account for the difference in the degree of the dissociation in these two solutions.

As stated above, all of these measurements both on carbon tetrachloride and carbon bisulphide solutions of the pentabro-



mide were made with the freshly prepared solutions, and no differences in color intensity were observable between the freshly prepared solutions and those that had stood for several hours; so that the dissociation equilibrium seems to be reached almost instantaneously, at least, at the dilutions investigated. We hope, however, to make further studies bearing upon this point. The effect of temperature and concentration on the progress of the change will also be studied in the case of solutions of phosphorus pentabromide, of phosphorus trichloridibromide,  $\text{PCl}_3\text{Br}_2$ , and of phosphorus trichloridiiodide,  $\text{PCl}_3\text{I}_2$ . The conduct of these last-named substances should prove especially interesting in this connection.

STATE COLLEGE OF KENTUCKY,  
LEXINGTON, Feb., 1899.

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## ON THE COLOR OF COMPOUNDS OF BROMINE AND OF IODINE.

BY J. H. KASTLE.

It is believed that the results already discussed in the preceding paper on the dissociation of phosphorus pentabromide will, if correctly interpreted, throw some light on the color of halogen compounds. So far as is known to the writer, no one has ever attempted an explanation of the remarkable relations as to color existing among the halogen derivatives. Ostwald<sup>1</sup> has attempted to account for the characteristic color of certain classes of salts in solution by the theory of electrolytic dissociation.

The present writer in 1894<sup>2</sup> called attention to certain difficulties encountered in endeavoring to apply the theory of electrolytic dissociation to the color of salts in solution, and advanced the view that such color could be better explained by supposing such substances to be hydrolyzed in solution whereby greater or less amounts of the colloidal modification of the base would be produced, and this being of itself colored would serve to impart the characteristic color of a given class of salts to the solution itself.

Carey Lea<sup>3</sup> has made the color of the ions of elements the

<sup>1</sup> Theory of Solutions, Eng. Ed., 268.

<sup>2</sup> This JOURNAL, 16, 326.

<sup>3</sup> Chem. News, 48, 203, 260, 271 (1896).



basis of a system of classification ; and from his study of the color relations of atoms, ions, and molecules he draws several conclusions, the most important of which for the discussion in hand is as follows :

“ When highly colored inorganic substances are composed of colorless ions, then if these substances can be brought into solution, the color wholly disappears. A number of instances are given above, and no exceptions were met with. Much that is important follows from this. It is proved that the ions have become so far separated that they no longer influence each others' vibration periods. For example, antimony pentasulphide is an intensely colored substance. It dissolves easily in solutions of alkaline sulphides, forming absolutely colorless solutions, because the ions of antimony and sulphur are colorless, and in the act of solution they separate sufficiently to no longer influence each others' vibration periods, without, however, passing out of each others' spheres of influence. The ion theory is the only one capable of explaining this loss of color ; and, on the other hand, the reactions are so exactly conformable to that theory that they constitute a new proof of its correctness.”

In another part of this paper Carey Lea cites mercuric iodide as an excellent illustration of the principle just stated, for the reason that while it is strongly colored in the solid state its solutions are colorless.

Quite recently Venable and Miller<sup>1</sup> have investigated the change in color of solutions of chromic salts from violet to green, and have adopted the explanation originally offered by Berzelius ; *viz.*, that the change in question is brought about by the formation of a soluble basic salt which itself is green in color. A number of explanations have been advanced also from time to time for the characteristic color of certain groups of organic dye-stuffs, but so far as the writer is aware no one has ever attempted to account for the color relations among halogen compounds, generally, or, to take a special case no one has ever made an attempt to account for the fact that lead bromide is white, while the iodide is yellow. The color relations existing among the halogen compounds are so well

<sup>1</sup> J. Am. Chem. Soc., 20, 484.

known as scarcely to require mention. In order that the subject may be clearly presented and for the purposes of argument, it will be well to enumerate them in this connection. In the first place, it should be clearly borne in mind that the halogen compounds of such elements and radicals as furnish colored compounds generally are beyond the scope of the present discussion; and that the same applies only to those colored compounds, the color of which seems certainly to be due to the presence of the halogen.

Omitting such compounds as those of the elements chromium, nickel, copper, cobalt, etc., and the halogen derivatives of such organic compounds as are in themselves dye-stuffs, or contain a chromogenic group, it would seem that the following general propositions could be laid down concerning the color of halogen compounds:

1st. Nearly, if not all, fluorine compounds are white; a few are colored. For example, bismuth fluoride is described as gray, and one modification of silver fluoride as yellow.

2nd. By far the greater number of chlorine compounds are white; a few, however, are yellow, for example  $\text{PCl}_5$ , and pentachlorophenolchloride,  $\text{C}_6\text{Cl}_5\text{OCl}$ .

3rd. By far the greater number of bromine compounds are white; a considerable number of them are yellow in color; some are red, and quite a number of perbromides are known having a red color.

4th. The greater number of iodine compounds also are white; a considerable number are yellow; and such as are darker in tint than the corresponding yellow bromine compounds, also a few iodides, are red, and a great many periodides are known which show a general resemblance in appearance to iodine in the solid state, and which by transmitted light exhibit the dark wine-red tints, characteristic of iodine in the liquid state and of solutions of this element.

5th. The color intensity of the halogens may be represented roughly at least, by the sign of greater or less,  $\text{F} < \text{I}$ , and the color intensity of their corresponding compounds, in some instances at least, may be similarly indicated,  $\text{MF} < \text{MI}$ .

The examples given in the following table will serve to illustrate the truth of these general propositions:

*Fluorine.*

White compounds.	Yellow compounds.	Red compounds.
$\text{CaF}_2, \text{PF}_5$		

*Chlorine.*

Tetrachlorquinone	$\text{PCl}_5, \text{C}_6\text{Cl}_6, \text{OCl}$
$\text{HgCl}_2, \text{NaCl}$	
$\text{NaCl}, \text{KCl}, \text{BaCl}_2$	
$\text{CaCl}_2, \text{AlCl}_3,$	
$\text{CHCl}_3, \text{AgCl}$	
$\text{PbCl}_2, \text{HgCl}$	
$\text{AsCl}_3, \text{SbCl}_3, \text{PCl}_3$	
$\text{C}_6\text{H}_5\text{SO}_2\text{NCl}_2, \text{C}_6\text{H}_5\text{OCl}$	
$\text{CCl}_4, \text{Cl}_2.5\text{H}_2\text{O}, \text{etc.}, \text{etc.}$	

*Bromine.*

$\text{KBr}, \text{NaBr}, \text{CaBr}_2$	$\text{AgBr}, \text{C}_6\text{H}_5\text{SO}_2\text{NBr}_2$	$\text{Br}.5\text{H}_2\text{O}$
$\text{BaBr}_2, \text{HgBr}_2, \text{PbBr}_2,$	$\text{C}_6\text{H}_5\text{B}_3\text{OBr}$	$\text{KBr}_3$
$\text{CHBr}_3, \text{CBr}_4, \text{PBr}_3$	$\text{HgBrI}, \text{PBr}_6$	
	$\text{CBrO}$	

*Iodine.*

$\text{KI}, \text{NaI}, \text{CaI}_2$	$\text{AgI}, \text{HgI}_2$	$\text{Cl}_4, \text{PI}_3$
$\text{BaI}_2, \text{etc.}$	$\text{HgBrI}, \text{PbI}_2,$	$\text{KI}_3, \text{HgI}_2$
	$\text{CHI}_3, \text{HgI}$	$\text{AsI}_3$

The gradation in color which is often observed among halogen compounds is well illustrated by the following series of compounds :

$\text{AgCl}$ —white	$\text{CHCl}_3$ —colorless
$\text{AgBr}$ —light yellow	$\text{CHBr}_3$ —colorless
$\text{AgI}$ —yellow	$\text{CHI}_3$ —very light yellow
$\text{CCl}_4$ —colorless	$\text{HgCl}_2$ —white
$\text{CBr}_4$ —colorless	$\text{HgBr}_2$ —white
$\text{Cl}_4$ —dark red	$\text{HgBrI}$ —very light yellow
	$\text{HgI}_2$ —yellow or red
$\text{PbCl}_2$ —white	$\text{PF}_5$ —colorless
$\text{PbBr}_2$ —white	$\text{PCl}_5$ —light yellow
	$\text{PBr}_5$ —yellow or red
$\text{PbI}_2$ —yellow	$\text{PI}_5$ —not known with certainty

From even these few examples one thing seems reasonably certain, and that is that the color relationships displayed among halogen compounds are not haphazard, nor mere coincidences, but are as much the subject of law and order as any other properties of compound substances. Whether any sat-

isfactory explanation can be offered for these relationships as to color remains yet to be seen. It is believed, however, that the color and general conduct of phosphorus pentabromide and similar compounds is such as to throw considerable light on this subject. Phosphorus pentabromide is a yellow crystalline compound slightly darker in tint than octahedral sulphur. It has been described as having a citron-yellow color. When this compound is heated in a sealed tube it becomes darker and more red in color and then melts to a red liquid, which at once dissociates, filling the tube with deep-red vapors, exactly the color of free bromine, and from these vapors the compound is deposited in beautiful crystalline condition on the colder parts of the tube. Now let us reverse this process, and start with a hot tube filled with the dissociated vapors of this compound, and so cool that the compound will first condense to a liquid, which will then solidify, giving us the yellow crystalline variety of the compound. The color is certainly such that on looking at a heated tube containing this substance in which the contents are gaseous no one could doubt for a moment that bromine as such is present in gaseous form, and that the red color of the gases is in reality due to this constituent. But this compound is also red in the liquid state. Hence, if we believe that the red color of this substance in the gaseous state is due to the presence of free bromine, it seems probable that free bromine is present in the substance in its liquid condition, or that it is dissociated in the liquid as well as in the gaseous condition, only not to as great an extent. Finally the red liquid solidifies and a yellow crystalline substance results. To what is the yellow color due? To free bromine or to the compound itself? If there is anything in common between the solid, liquid, and gaseous states, and the kinetic theory certainly indicates that there is a great deal in common between them, it again seems not improbable that this yellow color is due to bromine. It would certainly seem to be in keeping with our knowledge of the continuity of the gaseous liquid and solid states to suppose, if the dissociation of any substance takes place to a very large extent in the gaseous condition and also to a notable degree in its liquid state, that it will also occur in

smaller amount, at least, even in the solid state ; and, hence, if it can be shown that the color of the substance in the gaseous state is due to one of the products of its dissociation, and the same for its color in the liquid condition, it would seem to follow logically that any similar color it might possess in the solid state is due also to the presence of one of the products of dissociation in smaller amount than in the liquid or gaseous condition of the substance. All this, of course, implies that the color of the substance is essentially the same in tint in the solid, liquid, and gaseous states, or that the product of the dissociation producing the color is capable of exhibiting two distinct color tints. In the solid state the yellow variety of phosphorus pentabromide has but little, if anything, of the reddish tint of bromine. The question then is, is there anything in common between the yellow color of this compound and the color of free bromine, or, stated in still another way, does free bromine ever impart a yellow color? In the first place, bromine vapor has been described as yellowish-red, and it gets more highly colored on heating ; and then it is believed that the answer to this question is also to be found in the color of aqueous solutions of this element. It can scarcely be called in question that the bromine in aqueous solutions at ordinary temperatures is chemically in the free condition, for according to investigations of Löwig<sup>1</sup> even the orange-colored hydrate of this element is dissociated at all temperatures above 15° C. ; and yet it is a fact that an aqueous solution of bromine is altogether different in color from a solution of this element in such solutions as carbon bisulphide, chloroform, etc.

An aqueous solution of bromine has a pronounced yellow tint which is not observed in solutions of this element in organic solvents ; in fact, as was observed in this laboratory several years ago, very dilute aqueous solutions of bromine show the most striking resemblance to strong chlorine water when the two are compared in long porcelain tubes, so that bromine, which is free in a chemical sense, may exhibit a yellow color, which is very much the same in tint as the yellow color shown by such substances as phosphorus pentabro-

<sup>1</sup> Pogg. Ann., 14, 114 ; and 16, 375.



mide and other yellow compounds of bromine and iodine. This change in the color of aqueous solutions of bromine from red to yellow is also observed by adding potassium bromide to the solution. This of course might be interpreted to mean that potassium perbromide is produced which in solution has a lighter and more yellow color than bromine itself. This is doubtless true, but the question suggests itself at once what constitutes the difference in color between potassium bromide, which is white, and this compound, which has been described by Berthelot as being orange-colored? There can be but one answer to this question, and that is that the difference in color is due to the molecule of bromine which differs from the other atom of this element in the compound, in that it conducts itself like free bromine; and then again from what has been shown by Jakowkin<sup>1</sup> regarding the conduct of potassium periodide it is certainly probable that this compound  $\text{KBr}_3$  is largely, if not entirely, dissociated in its aqueous solution; so that in this case as with the bromine hydrate and aqueous solutions of bromine there is a characteristic chemical instability, and a yellow color, both of which are traceable to what we ordinarily call free bromine.

In this connection it should be borne in mind also that all that has been said regarding the yellow tint observable in free bromine applies with equal force to the element iodine. Very dilute aqueous solutions of iodine also exhibit a yellow tint in every way analogous to that observed in solutions of bromine; and the effect of adding potassium iodide to dilute aqueous solutions of iodide is to bring out this yellow color strongly.<sup>2</sup>

<sup>1</sup> Ztschr. physik. Chem., **13**, 539, and **20**, 19.

<sup>2</sup> The influence of potassium iodide on the color of an aqueous solution of iodine is very remarkable, as is also the influence of potassium bromide on the color of an aqueous solution of bromine. These two salts in concentrated solutions have the effect of doing away, to a large extent, with the reddish tints of iodine and bromine, and making solutions of these elements decidedly more comparable with a solution of chlorine in color. The attempt has been made to determine roughly the color intensity of chlorine, bromine, and iodine by comparing strong chlorine water with very dilute solutions of bromine and iodine in concentrated solutions of potassium bromide and iodide respectively. The following are the results of some preliminary work in this direction:

The chlorine water used contained 0.00594204 gram per cc.

The bromine water used contained 0.000499527 gram per cc.

The iodine water used contained 0.00022015 gram per cc.

The solution of potassium iodide contained 150 grams KI in 250 cc. aqueous solution.



It has also been observed in this connection that, if solid iodine is reduced to a fine powder and mixed with an inert substance, such as dry finely-divided silica, a mixture is obtained which exhibits a decidedly yellow color, although the reddish tint of the iodine is also observable. If now it can be assumed that a somewhat similar condition of things exists, within solid crystalline bromides and iodides, we have a satis-

The solution of potassium bromide contained 80 grams in 250 cc. solution.

The following are the results of experiments made on the color of the iodine solution :

0.05 cc. iodine solution, imperceptible in 20 cc. of water, gives a distinct yellowish coloration with 20 cc. KI solution.

0.1 cc. iodine solution, equivalent to 0.000022015 gram iodine, is scarcely perceptible in 20 cc. of water.

0.1 cc. iodine, equivalent to 0.000022015 gram iodine, is distinctly yellowish in 20 cc. concentrated solution of KI.

0.2 cc. iodine solution, easily perceptible in 20 cc. of water ; giving a sort of reddish-violet tint to the solution.

0.2 cc. iodine solution, darker yellow than that produced with 0.1 cc. iodine solution in 20 cc. solution of KI.

0.3 cc. iodine solution, equivalent to 0.000066045 gram iodine, had fully as much color in 20 cc. of KI solution as 20 cc. of the chlorine water, the latter containing 0.11884080 gram of chlorine. The general resemblance to chlorine water of such a solution of iodine in potassium iodide as this is quite striking, but, in addition to its distinct greenish-yellow tint, it also shows a reddish-brown tint, which makes it impossible to produce exactly the same shade in the two. According to this experiment, the color intensity of chlorine and iodine would be as 1 to 1799.

Similar experiments made with bromine gave the following results :

0.3 cc. bromine solution, equivalent to 0.000149858 gram bromine, imperceptible as compared with 20 cc. of water.

0.5 cc. bromine solution, perceptible in 20 cc. of water.

1 cc. bromine solution, easily perceptible in 20 cc. of water ; slight brownish color.

2 cc. bromine solution, equivalent to 0.000999 gram bromine in 18 cc. KBr solution had almost the same tint as 20 cc. of the chlorine water—this latter containing 0.1188408 gram of chlorine, the only difference observable in these two being a slight reddish tint in the bromine solution which was not observed in the chlorine water. According to this experiment the relative color intensity of chlorine and bromine would be as 1 to 118.

Hence we have for the relative coloring power of these three elements the following : Cl, 1 ; Br, 118 ; I, 1799.

From these numbers it will be seen that there is a much greater difference in coloring power between chlorine and bromine than between bromine and iodine, and that such indeed is the case, seems to be indicated by many facts pertaining to the color of these three elements. From the numbers above given it will be observed that the color intensity of bromine as compared with iodine is about in the ratio of 1 to 15. By comparing the amounts of bromine and iodine, which are the smallest quantities perceptible in 20 cc. of water, the ratio of the color intensity of these two elements was found to be as 1 to 13.6. So that it would seem to be not far from the truth to say that in coloring power iodine is fifteen times as great as bromine. In this connection it should be stated that Schütze has already called attention to the fact that in the case of analogous elements an increase in atomic weight is attended by a deepening of color. It will be seen from the above, however, that the increase in color intensity is greatly in excess of the corresponding increase in atomic weights.

factory explanation of a large number of facts pertaining to the color of these compounds. It has been demonstrated beyond question that there is a causal connection between the dissociation phenomena of compound substances and the affinity of the elements composing them. The affinities of elementary substances are inversely proportional to the ease with which their compounds undergo dissociation. We are in the habit of attributing the difference in the conduct of hydrochloric and hydriodic acids towards heat to the different affinities of chlorine and iodine for hydrogen. So in the same manner it has been observed that these halogen compounds are the more highly colored which are the least stable and whose elements are held in combination by weaker affinities.

A great number of samples could be furnished illustrating the truth of this statement. A few of the more striking instances are given in this connection :

$\text{PF}_3$ —colorless, compound stable.

$\text{PCl}_3$ —colorless, compound stable.

$\text{PBr}_3$ —colorless, compound stable.

$\text{PI}_3$ —red prisms ; melts at  $55^\circ \text{C}$ . and boils at higher temperatures with evolution of iodine.

$\text{TeCl}_4$ —colorless.

$\text{TeBr}_4$ —orange when cold, bright red while hot.

$\text{TeI}_4$ —black, gives off iodine when heated.

$\text{CdF}_2$ —white, stable.

$\text{CdCl}_2$ —white, stable.

$\text{CdBr}_2$ —white, stable.

$\text{CdI}_2$ —white and also brownish, brownish variety unstable.

$\text{PF}_5$ —colorless, stable.

$\text{PCl}_5$ —very light yellow, somewhat unstable.

$\text{PBr}_5$ —Light orange yellow, also red ; more unstable than chloride.

$\text{PI}_5$ —So unstable that existence is doubtful.

$\text{CCl}_4$ —colorless liquid, stable.

$\text{CBr}_4$ —white solid, partly decomposed at  $200^\circ \text{C}$ . with evolution of bromine.

$\text{CI}_4$ —red, must be kept out of air. Decomposed by heat into carbon and iodine, and by water to iodoform.

$\text{CHCl}_3$ —colorless, stable.

$\text{CHBr}_3$ —colorless, stable.

$\text{CHI}_3$ —greenish-yellow, unstable both toward light and heat.

The same relation between color and instability and the converse, is found to hold also among aromatic compounds. As is well known, substitution of halogens for hydrogen in the ring has been found to produce compounds of remarkable stability. They have also been found to be colorless in nearly all instances. On the other hand, when the halogen enters in a side-chain the compounds produced are frequently unstable and are also nearly always colored either yellow, orange, or red. The following are some of the examples of these two classes of compounds :

*Compounds Containing the Halogen in the Ring and Showing great Stability.*

Iodobenzene—colorless oil.  
 Hexachlorbenzene—white.  
 Hexabrombenzene—white needles.  
 Pentabrombenzenesulphonic acid—white plates.  
 Pentabrombenzenesulphonamide—white needles.  
*p*-Chlorbenzenesulphonamide—white needles.  
 Tribromphenol—white needles.  
 Tetrabromphenol—white needles.  
 Pentabromphenol—adamantine crystals.  
 Triiodoaniline—white needles.  
*p*-Diiodobenzene—nacreous scales.  
 Triiodophenol—white needles.  
 Diiodophenol—white glistening plates.  
 Diiodosalicylic acid—white.  
 Pentachlorphenol—white needles.  
 Diazobenzene bromide—white.  
 Diazotribrombenzene sulphate—colorless.

*Aromatic Compounds Containing the Halogen in the Side-chain and Exhibiting Greater or Less Instability.*

Tribromphenol bromide—light yellow.  
 Pentachlorphenol chloride—golden yellow.  
 Diazobenzene perbromide—yellow.  
 Diazotribrombenzene bromide—golden tablets.  
 Diazotribrombenzene perbromide—orange prisms.  
 Iodobenzene chloride,  $C_6H_5ICl_2$ —yellow needles. Begins to decompose at  $80^\circ C.$ , and decomposes completely at  $120^\circ C.$  into iodobenzene and chlorine.  
*p*-Bromiodobenzene dichloride—yellow needles, unstable.  
 Benzenedibromsulphonamide,  $C_6H_5SO_2NBr_2$ —orange yellow, melts with decomposition at  $110^\circ C.$   
*p*-Chlorbenzenedibromsulphonamide—yellow, unstable.

In view of the above, it can scarcely admit of doubt that the color and stability of halogen compounds are correlated properties, and probably traceable to the same cause, and therefore this question has suggested itself, Is there not some connection between the color of halogen compounds and their dissociation in the solid state? The facts enumerated above certainly seem to point to such a conclusion. Further, if the color of halogen compounds is in reality due to dissociation, then it follows that the color of any particular halogen compound ought to become deeper and more pronounced on heating; and such has been found to be the case. Lead iodide, mercuric bromide, silver iodide, silver bromide, iodoform, tribromphenol bromide, and benzenedibromsulphonamide all become more strongly and highly colored even under boiling water.

The effect of still higher temperatures on the color of some of these compounds has also been tried. All the substances experimented with were heated in small hard glass test-tubes.

*Silver Bromide.*—When silver bromide is heated it darkens to an orange color even while in the solid state. On still further heating it melts to a deep-red liquid of very much the same appearance as a solution of bromine.

*Silver Iodide.*—When this compound is heated it changes from yellow to orange and finally to a dark purplish-brown powder. It then melts to a deep reddish-brown liquid which closely resembles iodine in concentrated solutions of potassium iodide, or in the molten state. It is so dark in color as to be opaque except in thin layers, and it is decidedly darker in color than silver bromide in the molten state just as it is at ordinary temperatures. In cooling from the molten state it passes through a strikingly beautiful scarlet tint which is altogether similar to the red modification of mercuric iodide. At still lower temperatures it closely resembles a certain color displayed by molten sulphur.

*Lead Bromide.*—Lead bromide becomes light yellow when heated and then melts to a liquid which in color resembles sulphur in its first molten stages. This liquid becomes steadily darker as the heating is continued, and finally takes on a deep reddish-brown color which closely resembles that of a solution

of bromine and iodine ; and by continued and prolonged heating bromine is evolved. On cooling, lead bromide passes through the same changes of color in reverse order, and is finally obtained as a white substance again.

*Lead Iodide.*—This compound steadily darkens in color on being heated, passing through deepening shades of orange up to brownish-crimson of great depth of color. It then melts to a dark brownish-red solution which strongly suggests the color of bromine or iodine ; and at the same time vapors of iodine make their appearance in the tube.

*Mercuric Bromiodide*,  $\text{HgBrI}$ .—This compound has a pale yellow color in the cold. On being heated it becomes darker yellow, then orange, and finally melts to a reddish liquid, resembling a solution of bromine or molten sulphur in some of its phases. This compound has been found to sublime unchanged if the heating is continued.

*Mercuric Iodide*,  $\text{HgI}_2$ .—The conduct of this compound when heated is of special interest in this connection. When the red variety of this substance is heated, it seems to get darker in color up to a certain point, taking on a reddish-brown tint, which is not observable in the cold, and then very suddenly it changes to the yellow modification. In this connection it is interesting to note that the color of the yellow variety of mercuric iodide is deeper yellow, even in the cold, than that of the bromiodide. On heating the yellow modification of mercuric iodide it becomes darker, and then melts to a light-reddish liquid ; this rapidly increases in depth of color as the heat is applied until it becomes dark port-wine red, like solutions of iodine in potassium iodide ; and at high temperatures in the liquid condition it is difficult to distinguish mercuric iodide from liquid bromine, so far as color and opacity are concerned. It should be observed in this connection that at corresponding temperatures mercuric iodide is always of a deeper and darker tint than the bromiodide, and the same is also true of the other iodides and bromides examined.

*Cadmium Iodide.*—One modification of this compound exists in the form of beautiful, white scales. When this modification of the compound is heated in a tube it becomes light yellow.



low in color, and then melts to a clear reddish-brown liquid, which becomes darker in color and more opaque, the higher it is heated, and finally vapors of iodine appear in the tube.

What is the significance of these results? Is it not that the dissociation begun in the compound in the solid state<sup>1</sup> at the lower temperature simply becomes augmented with the rise of temperature, thereby increasing the color? It is certainly a well-established truth that such is the effect of heat on the dissociation process wherever it has been observed. And if the color of halogen compounds is in reality due to their dissociation in the solid state, then their conduct on heating is just such as would be demanded by the theory. In fact the only break in the continuity of the process, observable on heating the above-named compounds, is the change from the crystalline to the liquid condition and vice-versa.<sup>2</sup> So far as the accompanying change of color is concerned it is gradual and has been found to be essentially the same in variation of tint as is observed in passing through certain aqueous solutions of bromine and iodine of various dilutions.

Let us consider the conduct of lead iodide specifically in the light of this hypothesis. In the liquid state at high temperatures this compound exactly resembles a concentrated solution of potassium periodide. Now it is generally conceded that potassium periodide is largely dissociated in aqueous solutions, and that its color is due to the iodine resulting from this dissociation, and it is further certain that the one molecule of the iodine it contains conducts itself chemically as though it

<sup>1</sup> Richards, in a recent communication on "The Cause of the Retention and Release of Gases Occluded by the Oxides of Metals," has found it necessary to assume that copper oxide is slightly dissociated at red heat; and that auric oxide and silver oxide probably dissociate at comparatively low temperatures. This JOURNAL, 20, 701.

<sup>2</sup> It is not intended to confuse the dissociation of halogen compounds here under discussion with the electrolytic dissociation of salts, but it is interesting to note that according to LeBlanc, "Many salts possess not inconsiderable conductivities below their melting-points as well as above," *Electro-Chemistry*, pp. 119-120; and that according to Graetz, "No sudden change in the conductivity of a salt or of its temperature coefficient, is observable at its melting-point" [*Wiedemann's Ann.*, 40, 18, (1890)]. "From this it must, apparently, be concluded," according to Nernst, "that there is no marked change either in ion friction, or in the electrolytic dissociation, in the liquefaction of a salt" (*Theoretical Chemistry*, Translation, p. 593). So also on heating halogen compounds, as will be seen in the above, no sudden or marked changes of color are observable, but simply a gradual increase in the depth of tint.



were in the free condition. Therefore, if the color of liquid lead iodide at high temperatures is similar to that of potassium periodide, would not the assumption be justifiable, that this compound is also dissociated at these temperatures. Further, on cooling lead iodide, no sudden break or variation in the color is observable, but it passes by insensible gradations through varying shades of reddish-brown, brownish-crimson, reddish-orange, orange, to yellow; and all of these tints can be imitated by solutions of the element iodine in potassium iodide. Therefore, is it not logical to conclude that the dissociation of lead iodide in the liquid state falls off by insensible gradations until a minimum, but still appreciable, amount is reached in the cold solid? Such certainly would seem to be the case.

Then again, as is well known, lead bromide and lead iodide have nothing in common in color in the solid state, the bromide being pure white, and the iodide yellow. When heated, however, the bromide becomes yellow; the color gradually increases in intensity the more strongly the substance is heated. In other words, by the action of heat it can be made to resemble the iodide in color. In fact, the more strongly these two compounds are heated the more closely do they resemble each other. On the supposition that the color of lead bromide is constitutive, that is, that it is peculiar to the molecule  $\text{PbBr}_2$ , as such, we have no satisfactory explanation of its changes of color on heating, and there is no reason for its showing a resemblance in color to lead iodide at high temperatures. On the supposition that the color of the halogen compounds is due to dissociation, however, we have a satisfactory explanation of these phenomena. In the solid state lead bromide is not dissociated at all, whereas the iodide is to some extent; hence, the former is white while the latter is yellow. As the lead bromide is heated, however, it begins to dissociate, and hence exhibits a yellow color at once. As the temperature is raised, this dissociation increases in amount, and the melted compound looks more and more like lead iodide in the molten state. Furthermore, according to these suppositions, lead bromide, if it changes in color at all, must take on a color resembling that of the iodide, in consequence

of the fact that bromine and iodine themselves closely resemble each other in color, at least under some conditions. This also has been found to be true. In other words, all changes in the color of halogen compounds partake of the nature of additive properties in general, and hence must receive a similar explanation.

There is one other point in this connection which deserves mention, and that has reference to the extent of the dissociation occurring in colored halides in the solid state. At the present stage of our knowledge it is entirely impossible to measure this with any degree of certainty. It should be said, however, in this connection, that the amount of this dissociation must be extremely small. By reference to the foot-note on page 405 it will be seen that 0.000066045 gram of iodine serves to impart a decided yellow color to 20 cc. of a solution of potassium iodide containing 150 grams of potassium iodide in 250 cc. of solution, and having a specific gravity of 1.41; so that this extremely small amount of iodine serves to color at least 28 grams of substance a decided yellow. This corresponds to about 66 parts of iodine in 28 million parts of substance, or to nearly 2.4 parts of iodine per million. If, therefore, only this extremely small amount is necessary to impart a decided yellow color to such a solution, it would seem reasonably certain that the amount of this element necessary to impart such a color as is usually observable in its colored compounds must also be extremely small; and, therefore, that the degree of dissociation of such compounds is also extremely small—so small in fact that it could not be measured except by some colorimetric method.

In conclusion, it must be admitted that the halogens impart a characteristic color to a large number of their compounds. According to Bernthsen<sup>1</sup> "most organic compounds are colorless." "Compounds containing iodine, however, are frequently yellow or red." This characteristic color must be either an additive or a constitutive property. Either the color must be due to the influence exerted by the halogen as a component part of the molecule on the molecule as a whole, *i. e.*, it must be a constitutive property, or the color must be

<sup>1</sup> Organic Chemistry, Eng. Ed., p. 31.

due to the dissociation of a small number of the molecules of the substance whereby a very small amount of the halogen becomes free and assumes its own color, and thereby imparts its characteristic tint to the compound as a whole. On the former assumption it would certainly prove a difficult task to account for the fact that hydriodic acid, containing 99.2 per cent of iodine, is colorless, whereas a great many periodides containing less than 50 per cent of iodine are so highly colored as to resemble the element iodine itself. On the latter assumption, however, this would simply mean that the affinity of hydrogen for iodine is such as to render the dissociation of hydriodic acid impossible at ordinary temperatures; hence the compound is colorless. On the other hand, as is well known, the periodides as a class are very unstable, and hence are strongly colored in consequence of considerable dissociation, even in the solid state. It is therefore believed that the hypothesis under discussion has much to recommend it on the score of simplicity, and that it derives support from a great number of facts; and should it prove to be correct, it would considerably enlarge our physical and chemical conceptions of the solid state.

Mr. A. S. Loevenhart has been of great assistance to me in the preparation of this article, and I desire to thank him in this connection.

STATE COLLEGE OF KENTUCKY,  
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Contributions from the Sheffield Laboratory of Yale University.

LXX.—ON THE FORMATION OF POTASSIUM  $\beta$ -FERRICYANIDE THROUGH THE ACTION OF ACIDS UPON THE NORMAL FERRICYANIDE.

BY JAMES LOCKE AND GASTON H. EDWARDS.

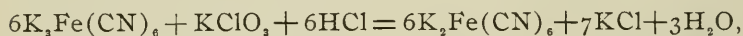
We have shown in a previous paper<sup>1</sup> that when a solution of potassium ferricyanide is heated for a short time with potassium chlorate and hydrochloric acid, an isomer of this salt is obtained, which crystallizes with one molecule of water. This salt had already been obtained by Skraup<sup>2</sup> and others,

<sup>1</sup> This JOURNAL, 21, 193.

<sup>2</sup> Ann. Chem. (Liebig), 189, 368.

in an impure state, by the action of oxidizing agents, and was regarded by them as an oxidation-product of the normal ferricyanide, with the formula  $K_2Fe(CN)_6$ . At the time of our first investigation, we likewise ascribed its formation to the oxidizing action of the potassium chlorate, but have since found that it is due to the hydrochloric acid alone, and is, in fact, formed more or less readily by the action of any acid on potassium ferricyanide. Its preparation by former experimenters can thus be readily explained, as their operations were all carried on in acid solutions.

In our first experiments to investigate this point we used the same quantity of hydrochloric acid as in the preparation of the salt with potassium chlorate, that is, the amount required according to the equation given by Skraup,



and otherwise performed the experiments exactly as described in our previous article. 50 grams of potassium ferricyanide were dissolved in 100 cc. of water, heated to boiling, and 18 cc. of concentrated hydrochloric acid (sp. gr. 1.19), diluted with three times their volume of water, were added, and the mixture allowed to stand on the water-bath. Small portions were taken out at short intervals, cooled, precipitated with equal volumes of 95 per cent alcohol, and the precipitates filtered off. These various preparations were then tested with bismuth nitrate, with which the  $\alpha$ -ferricyanide gives a yellow precipitate, and the  $\beta$ -ferricyanide none. Subsequently, the percentages of cyanogen which they contained were determined by reduction with sodium amalgam, and titration to potassium  $\alpha$ -ferricyanide with potassium permanganate.<sup>1</sup>

Two samples of the solution, taken out after the reaction had proceeded one and one-half minutes and three minutes, respectively, gave with alcohol yellow and yellowish-green precipitates, the colors of which were due to the presence of unchanged  $\alpha$ -ferricyanide. These showed, with bismuth nitrate, the test characteristic of the latter. At the end of five minutes the originally reddish-yellow solution had assumed the peculiar red-violet color of the  $\beta$ -salt, and the precipitated

<sup>1</sup> This JOURNAL, 21, 193.





FIG. I.—Potassium  $\beta$ -ferricyanide.

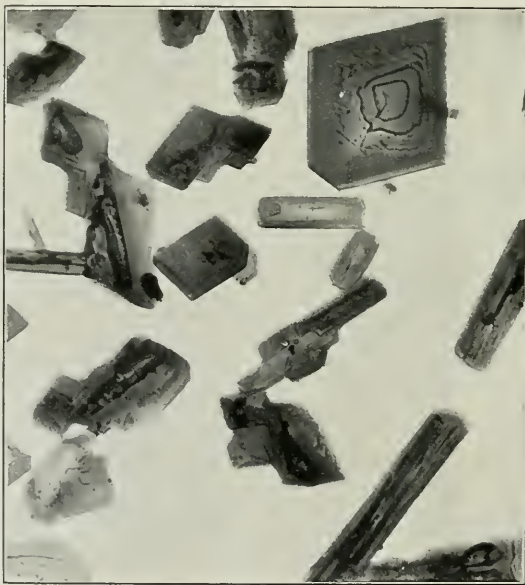


FIG. II —Potassium  $\alpha$ -ferricyanide.



samples then consisted of a completely homogeneous mass of well-formed, olive-green crystals. These showed all the properties of potassium  $\beta$ -ferricyanide,  $K_3Fe(CN)_6 \cdot H_2O$ , as previously described by us. They are most readily recognized by their very characteristic crystal-habit showing the forms illustrated in Fig. I. This is taken from a photomicrograph, as is also Fig. II, which shows crystals of the normal ferricyanide obtained under similar conditions. At the same time the percentage of cyanogen rapidly fell to a value corresponding closely to that calculated for the  $\beta$ -salt; that is, 44.96 per cent. The sample obtained after the reaction had proceeded for ten minutes was of a greenish-black color, and showed no distinct crystallization, indicating that further decomposition had taken place. In this, and subsequent samples also, the percentage of cyanogen had fallen considerably below the value for the  $\beta$ -compound.

The analytical results of this series of experiments are tabulated below.

#### Series A.

50 grams  $K_3Fe(CN)_6$ : 18 cc. conc. HCl.

1 cc.  $KMnO_4$  solution = 0.03704 gram  $K_3Fe(CN)_6$ .

No.	Time. Min.	Color.	Weight of sub- stance taken. Gram.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6 \cdot H_2O$ .	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$ .	Cyanogen found.
I	1½	yellow	0.1881	4.9	4.81	5.08	45.74
II	3	yellowish-green	0.2616	6.8	6.7	7.06	45.65
III	5	olive	0.2073	5.3	5.31	5.59	44.89
IV	7½	"	0.2919	7.4	7.47	7.88	44.52
V	10	green-black	0.2376	5.9	6.08	6.42	43.60
VI	15	"	....	...	...	...	....
VII	20	"	0.3014	7.3	7.71	8.17	42.53

Cyanogen calculated for  $K_3Fe(CN)_6$ , 47.41 per cent.

" " "  $K_3Fe(CN)_6 \cdot H_2O$ , 44.96 per cent.

The question next suggested itself, whether it was necessary to have hydrochloric acid present in definite molecular quantity, as above, or whether its action was not merely one

of catalysis, and caused by the presence even of small quantities. In order to decide this, experiments similar to the above were made, in which one-half, one-fourth, and one-eighth of the amount of the acid there used was employed. It was found, not only, that the  $\beta$ -compound was formed in each case, but that its subsequent decomposition by the acid takes place much more slowly than when the acid is more concentrated. The reactions could, therefore, be much more easily followed in these experiments, as a considerable interval elapsed between the point at which the  $\alpha$ -salt disappeared and that at which the  $\beta$ -salt noticeably began to decompose. The results of these experiments are tabulated below :

*Series B.*

50 grams  $K_3Fe(CN)_6$ ; 9 cc. conc. HCl.

No.	Time. Min.	Color.	Weight of sub- stance taken. Gram.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$ $H_2O$ .	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$ .	Cyanogen found.
I	5	yellowish-green	0.2152	5.6	5.51	5.81	45.74
II	10	olive	0.2222	5.7	5.68	5.9	45.03
III	15	"	0.2233	5.7	5.72	6.03	44.82
IV	20	green-black	0.2155	5.2	5.52	5.82	42.37
V	25	"	0.2393	5.7	6.12	6.49	41.83

*Series C.*

50 grams  $K_3Fe(CN)_6$ ; 4.5 cc. conc. HCl.

I	2	yellow	0.3535	9.3	9.05	9.54	46.19
II	4	yellowish-green	0.3421	8.9	8.75	9.24	45.68
III	6	olive	0.1901	4.9	4.86	5.13	45.26
IV	8	"	0.2569	6.6	6.57	6.94	45.11
V	10	"	0.2263	5.8	5.79	6.11	45.00
VI	15	"	0.2223	5.7	5.69	5.9	45.03
VII	20	green	0.1994	5.0	5.1	5.38	44.03
VIII	25	green-black	0.3195	8.0	8.18	8.63	44.00
IX	30	"	0.2198	5.5	5.63	5.93	43.94

## Series D.

50 grams  $K_3Fe(CN)_6$ ; 2.25 cc. conc. HCl.

No.	Time. Min.	Color.	Weight of substance taken. Gram.	Cc. $KMnO_4$ used.	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$ , $H_2O$ .	Cc. $KMnO_4$ calculated for $K_3Fe(CN)_6$ .	Cyanogen found.
I	5	yellow	....	..	...	...	....
II	10	"	0.2256	5.9	5.77	6.06	45.92
III	15	yellowish-green	0.1510	3.9	3.86	4.08	45.02
IV	20	olive	0.2121	5.4	5.43	5.73	44.71
V	25	"	0.2584	6.6	6.61	6.98	44.85
VI	35	"	0.2639	6.7	6.75	7.12	44.57
VII	45	"	0.2113	5.3	5.41	5.7	44.04
VIII	55	green	0.2036	5.0	5.21	5.5	43.12
IX	65	green-black	0.2171	5.4	5.55	5.86	43.67
	Hours.						
X	1 $\frac{1}{2}$	"	0.1745	4.2	4.46	4.71	42.27
XI	2	"	0.2015	4.9	5.17	5.42	42.70
XII	2 $\frac{1}{2}$	"	0.2010	4.5	5.14	5.43	39.31

In Series *D* it will be seen that in the first fifteen minutes the percentage of cyanogen fell from the value calculated for the  $\alpha$ -salt, or 47.41 per cent, to 45.02 per cent, or nearly the value calculated for the  $\beta$ -salt, a loss of 2.4 per cent. From this point on, the precipitated samples gave no reactions with bismuth nitrate. During the next twenty minutes the percentage of cyanogen fell only 0.45 per cent, and the fractions taken out in this interval were all thoroughly homogeneous and well crystallized. Beyond this point the decomposition again became more rapid, and the samples obtained were of far less satisfactory appearance than those in numbers III-VI.

In Series *B* and *C* similar results were obtained, but the reactions proceeded much more rapidly. In *C*, for instance, the samples ceased to react with bismuth nitrate in eight minutes, and the  $\beta$ -salt was noticeably decomposed at the end of twenty minutes. It must, therefore, be concluded that the velocity of the reaction is directly dependent upon the concentration of the acid.

Similar results were obtained when other acids were substituted for hydrochloric acid. Experiments were instituted

with sulphuric, oxalic, and acetic acids. No quantitative determinations were made, however, as it was found impossible, in the first two cases, to obtain the precipitates free from potassium sulphate and potassium oxalate. But that the reaction proceeded in the same way as when hydrochloric acid was used, was readily recognized by the color of the solution and by the appearance of the precipitates. With oxalic acid the  $\beta$ -salt was formed less readily than with sulphuric acid, though in both cases the conversion of the  $\alpha$ -salt into its isomer took place more slowly than it did in hydrochloric acid solution. It would thus appear that the catalytic action of different acids, to which the formation of the  $\beta$ -salt is due, is directly dependent upon the degree to which the acid used undergoes ionization. According to this, an acid such as acetic, which ionizes but slightly, should have only a very slow action. This was found to be the case, for with dilute acetic acid we could obtain no  $\beta$ -salt at all, and a solution of ferricyanide, heated for an hour with the concentrated acid (2 molecules), still gave a slight precipitate with bismuth nitrate.

NEW HAVEN, February, 1899.

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Contributions from the Chemical Laboratory of Harvard College.

## CXI.—TRINITROPHENYLMALONIC ESTER.<sup>1</sup>

[SECOND PAPER.]

BY C. LORING JACKSON AND J. I. PHINNEY.

The work described in this paper was undertaken with the intention of preparing some derivatives of the trinitrophenylmalonic ester (picrylmalonic ester),



discovered by C. A. Soch and one of us.<sup>2</sup> It has led to the discovery of a second and more stable form of the trinitrophenylmalonic ester, which melts at  $64^\circ$  instead of  $58^\circ$ , the melting-point of the form at first obtained; and we have also prepared the nitrite of this ester,



<sup>1</sup> Presented to the American Academy of Arts and Sciences, October 20, 1898.

<sup>2</sup> This JOURNAL, 18, 133.

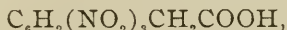
melting at  $109^{\circ}$ , the corresponding trinitrophenyltartronic ester,



melting at  $117^{\circ}$ , its acetyl derivative,



which melts at  $125^{\circ}$ , and the trinitrophenylacetic acid,



melting at  $161^{\circ}$ .

*The Two Modifications of Trinitrophenylmalonic Ester.*

The trinitrophenylmalonic ester, as prepared by Soch and one of us,<sup>1</sup> crystallized from alcohol in white, long, rather slender, rectangular plates, or when better developed in thick prisms with blunt ends, often as much as 2 centimeters long. It melted at  $58^{\circ}$ .<sup>2</sup> When we first took up the work again, we also obtained the trinitrophenylmalonic ester exclusively in this form, and confirmed repeatedly the observations given above on its crystalline form and melting-point. Somewhat later we converted a sample of the trinitrophenylmalonic ester into its very characteristic ammonium salt, and upon acidifying this and recrystallizing the ester thus set free we obtained instead of the rectangular plates four- (or six-) sided plates in which two of the opposite angles were unlike,—one being obtuse and the other acute,—so that the crystals were shaped somewhat like a kite; and not only did the form of these crystals differ in such a marked way from the rectangular plates previously obtained, but they also melted at  $64^{\circ}$  instead of  $58^{\circ}$ . During this experiment a solution of the ester from one of our preparations of it was evaporating spontaneously on the desk; the next morning these kite-shaped crystals were deposited from it, although it had previously yielded only the rectangular plates melting at  $58^{\circ}$ , and since then we have obtained from all our preparations only the form melting at  $64^{\circ}$ , whereas before exactly similar preparations had given

<sup>1</sup> *Loc. cit.*

<sup>2</sup> In the previous paper this melting-point is given as  $59^{\circ}$ , but it must be changed to  $58^{\circ}$ , as it was found after that paper was published that the zero point of the thermometer used had changed.

us exclusively the form melting at  $58^{\circ}$ , as has already been stated. Varying the conditions of the preparations, such as carrying them on in cooled or warmed solutions, or with longer or shorter standing, did not modify the result, so that we have not succeeded in adding to the stock of the modification melting at  $58^{\circ}$ , which we had on hand, when we encountered the other form.

The following experiment seems to us to suggest a possible explanation of these results : a solution of the form melting at  $58^{\circ}$  was evaporated until it began to deposit the rectangular crystals, and then inoculated with a speck of the form melting at  $64^{\circ}$ , when at once the kite-shaped crystals of this form began to appear, and no more rectangular crystals were produced. This experiment was tried several times early in our work ; it could not be repeated later, as then recrystallization alone of the form melting at  $58^{\circ}$  was enough to convert it partially or even completely into the form melting at  $64^{\circ}$ . As then a small amount of the form melting at  $64^{\circ}$  is enough to convert a large quantity of the other form into this, it seems probable that the small amount of the more stable form floating in the air of the laboratory as dust was enough to bring about this change, and to give us this more stable modification as the sole product of our preparations, and even of recrystallizations of the less stable form. The view that the inoculation of the solutions proceeded from the dust in the air is supported by the following observations : A preparation made with new apparatus and fresh material, but in the laboratory where these experiments had been tried, yielded only the stable form melting at  $64^{\circ}$ . Crystallizations of the form melting at  $58^{\circ}$  gave, after the work had been in progress some time, the form melting at  $64^{\circ}$ . We then crystallized a specimen melting at  $58^{\circ}$  in a fresh room, which had not been used for these experiments, and obtained in this way the rectangular plates melting at  $58^{\circ}$  ; but upon recrystallizing the specimen, the form melting at  $64^{\circ}$  appeared, and after this the first crystallization of a fresh specimen melting at  $58^{\circ}$  in this room gave crystals of the form melting at  $64^{\circ}$ . A probable explanation of these latter observations is that there was a little dust of the more stable modification in this room coming



from the clothes of one of us, who used it as a lecture-room, and that this was sufficient gradually to inoculate the solutions. As the laboratory building, apparently contaminated with the dust of the more stable form, seemed to offer little chance of preparing more of the form melting at  $58^{\circ}$ , we postponed publishing this paper for some years, in the hope that one of us (who left Cambridge at the end of the year) might prepare more of the form melting at  $58^{\circ}$  by working in entirely new surroundings. Unfortunately, the pressure of other duties has prevented the carrying out of this work, and we have decided that it is wiser to publish now the results already obtained rather than to postpone the appearance of the paper to a still later date.

The conversion of the form melting at  $58^{\circ}$  into that melting at  $64^{\circ}$  has been brought about by us in the following ways: By its conversion into the ammonium salt and setting free the ester by acidification;<sup>1</sup> by inoculating a saturated alcoholic solution with a crystal of the form melting at  $64^{\circ}$ ; by melting the less stable form it was partially changed into that melting at  $64^{\circ}$ , and, if the melting was repeated, the change became complete. It is possible, however, that this change might have been due to inoculation from dust. On the other hand, we have not succeeded in converting the form melting at  $64^{\circ}$  into that melting at  $58^{\circ}$  in spite of many experiments; even melting the more stable form and stirring it with a rod tipped with the modification melting at  $58^{\circ}$  did not have the desired effect.

The substance melting at  $64^{\circ}$  was purified by crystallization from alcohol, and after being dried *in vacuo* was analyzed with the following results:

I. 0.2050 gram of the substance gave, on combustion, 0.3149 gram of carbonic dioxide and 0.0736 gram of water.

II. 0.2007 gram of substance gave 0.3078 gram of carbonic dioxide and 0.0789 gram of water.

III. 0.2040 gram of substance gave 20.5 cc. of nitrogen at a temperature of  $21^{\circ}$  and a pressure of 759.6 mm.

<sup>1</sup> In my earlier work with Soch, the sodium salt yielded, on acidification, the ester melting at  $58^{\circ}$ .—C. L. J.

	Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$ .	I.	Found. II.	III.
C	42.05	41.89	41.82	....
H	3.50	3.98	4.36	....
N	11.32	....	....	11.41

The combustion of this substance must be carried on as slowly as possible, as it has a strong tendency to explode.

The molecular weight of the substance was also determined by the method of Raoult with the following results :

I. Weight of benzol used 19.2120 grams. Substance 0.3291 gram. Reduction of freezing-point  $0^\circ.230$ .

II. Weight of benzol used 15.7244 grams. Substance 0.3428 gram. Reduction of freezing-point  $0^\circ.306$ .

III. Weight of benzol used and weight of substance the same as in II. Reduction of freezing-point  $0^\circ.297$ .

	Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$ .	I.	Found. II.	III.
Molecular weight	371	365.1	349.0	359.6

From these results there can be no doubt that the preparation melting at  $64^\circ$  was trinitrophenylmalonic ester.

It is worth while to point out here that the form melting at  $58^\circ$  could not have owed its peculiarities in melting-point and crystalline form to the presence of a small quantity of some impurity, since it was repeatedly brought to a constant melting-point both by Dr. Soch and by us ; and, if this explanation were correct, this form should have been the first product of the preparations in our later work, whereas, after we had once obtained the form melting at  $64^\circ$ , we could not prepare the other. Dr. Soch's analyses of the form melting at  $58^\circ$  also show that it was pure.

	Calculated.		Found.
N	11.32	11.75	11.38

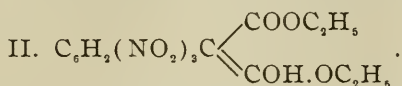
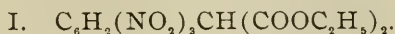
We are therefore led to the conclusion that the trinitrophenylmalonic ester exists in two isomeric forms.

The isomerism of these two forms is probably due to the same cause as that of the red and yellow anilidotrinitrophenyltartronic esters (melting at  $143^\circ$  and  $122^\circ$ ) discovered by W. B. Bentley<sup>1</sup> and one of us. It seems more doubtful whether it is related to the isomerism of the formylphenylacetic esters

<sup>1</sup> This JOURNAL, 14, 348.

discovered by W. Wislicenus,<sup>1</sup> of the dibenzoylacetones<sup>2</sup> and the benzoates of oxymethylenacetone<sup>3</sup> of Claisen, and the benzanilinacetacetic esters of R. Schiff,<sup>4</sup> since both of our isomers can be dissolved in alkaline solutions without alteration, whereas one of the most marked differences between the isomers in these other cases consists in the fact that one dissolves in alkalis and the other does not.

Our present knowledge of these substances is not sufficient to allow us to make a final statement in regard to the cause of this isomerism, but the following discussion is given for what it is worth. The fact that each form has been converted into a salt, and set free from this unaltered upon acidification, would indicate that it is a case of chemical rather than physical isomerism; and, if this is true, as the symmetrical nature of the substance would forbid stereomeric isomers, the only probable explanation which we have been able to find is that the isomerism depends on differences of structure in the malonic group, as indicated by the following formulas:



In other words, that the isomerism is analogous to that of the bodies studied by W. Wislicenus, Claisen, and R. Schiff. There are, however, objections to this explanation, and, as we have said already, the whole subject needs further investigation before any satisfactory theory can be found.

*Properties of the Trinitrophenylmalonic Ester Melting at 64°.*

—Crystallized from alcohol, it forms white plates, usually bounded by four or six sides. In the four-sided form there are two unlike opposite angles, one obtuse, the other acute, which give a very characteristic appearance to the crystals. The six-sided form is produced by two planes truncating the similar angles in the four-sided form. Both these forms resemble a kite in shape. Occasionally much more complex crystals were observed, having a parallel-sided projection arising from the middle of the obtuse end, and also terminated by

<sup>1</sup> Ber. d. chem. Ges., **28**, 767.

<sup>2</sup> Ann. Chem. (Liebig), **277**, 188.

<sup>3</sup> Ber. d. chem. Ges., **35**, 1785.

<sup>4</sup> *Ibid.*, **31**, 601.

an obtuse angle; this form had a general resemblance to the "spade" in playing cards. The plates were often thick, especially when having the complex form last described. The substance turns yellow on long exposure to the air, and imparts to alcohol a marked crimson color, which also has been observed on the ground-glass stopper of the bottle in which it was kept. In this case the color may have been due, however, to some alkali from the glass, but this was not the case in the alcoholic solution, as the color was only partially discharged by acidification. The modification melting at  $58^{\circ}$  forms similar crimson solutions. It melts at  $64^{\circ}$  to a red liquid. Its solubility in the organic solvents is essentially the same as that of the form melting at  $58^{\circ}$ ; that is, it is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less so in carbonic disulphide; soluble in cold alcohol, freely in hot, rather more soluble in methyl than in ethyl alcohol; insoluble in ligroin, or cold water, slightly soluble in hot water.

The action of acids upon this more stable trinitrophenylmalonic ester is described in some of the following paragraphs of this paper. Alkalies give with it dark-red salts, which crystallize well. The ammonium salt is especially characteristic; it was made by adding an excess of aqueous ammoniac hydrate to a warm, nearly saturated, alcoholic solution of the trinitrophenylmalonic ester. The solution took on a deep purplish-red color, and in a few seconds the whole solidified to a thick semisolid mass having the purplish-red color and consistency of clotted blood. A microscopic examination showed that this mass was made up of long, very slender, hair-like crystals, which, after drying, had a rich golden-brown color and a silky luster. The salt decomposed below  $100^{\circ}$ , at first turning black, but afterward melting to a clear, yellowish liquid, which exploded at higher temperatures. It is rather sparingly soluble in water, soluble in alcohol, chloroform, or acetone, insoluble in ligroin. The solutions have a dark-red color, but if the solution in water or alcohol is boiled for some time it turns yellowish-brown; unfortunately no product could be obtained from such solutions in a state fit for analysis.

An aqueous solution of the ammonium salt gave the following characteristic precipitates :

With salts of *barium* an abundant, crystalline, amethystine precipitate.

With salts of *strontium* a dark-red precipitate.

With salts of *calcium* a brick-red precipitate.

With salts of *zinc* an abundant, crystalline, scarlet precipitate, turning to reddish-brown on standing.

With salts of *cadmium* a granular, scarlet precipitate.

With salts of *copper* a heavy, flaky precipitate, varying from reddish-yellow to brownish-red.

With salts of *lead* heavy, dark-red flocks.

Salts of the other metals gave precipitates as a general rule, but they were not characteristic. The behavior with argentic nitrate, however, should be especially mentioned, as this gave no precipitate in dilute solutions, and only a slight, cloudy, dark-red one when the solutions were strong. The barium, zinc, and copper salts were analyzed.

*Barium Salt.*—This salt was made by adding a solution of baric chloride to the aqueous solution of the ammonium salt. The heavy purple flocks thus obtained were washed with water, dried at 100°, and analyzed with the following result :

0.4864 gram of the salt gave 0.1236 gram of baric sulphate.

	Calculated for	Found.
	$[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{C}(\text{COOC}_2\text{H}_5)_2]_2\text{Ba}$ .	
Ba	15.62	14.95

The salt is so hygroscopic that 0.2 gram will gain as much as 4 milligrams during the time of weighing, if it is in an open watch-glass. In evaporating it with sulphuric acid for analysis, care must be taken not to apply the heat too suddenly at first, or an explosion may result. The best plan is to heat the mixture for some time to 100°, as then the decomposition goes on quietly.

*Properties.*—The barium salt appears as a purple, obscurely crystalline mass, essentially insoluble in water. It explodes if heated to 120°.

*Zinc Salt.*—This salt was made by mixing solutions of zincic sulphate and the ammonium salt of the ester. It was purified by washing, dried at 100°, and analyzed with the following result :



0.4869 gram of the salt gave 0.0478 gram of zinc oxide.

	Calculated for	Found.
	$[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{C}(\text{COOC}_2\text{H}_5)_2]_2\text{Zn}$	
Zn	8.07	7.88

*Properties.*—The zinc salt forms a reddish-prown crystalline mass, essentially insoluble in water, but very hygroscopic. Like the barium salt it explodes easily, if heated with strong sulphuric acid, and therefore the same precautions must be used in analyzing it which were recommended in the case of the barium salt.

*Copper Salt.*—This salt was made by mixing aqueous solutions of cupric sulphate and the ammonium salt of the ester. It was purified by washing with water, and after drying at  $100^\circ$  gave the following result on analysis :

0.3012 gram of the salt gave 0.0291 gram of cupric oxide.

	Calculated for	Found.
	$[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{C}(\text{COOC}_2\text{H}_5)_2]_2\text{Cu}$	
Cu	7.92	7.72

*Properties.*—The copper salt is a brownish-red powder, essentially insoluble in water. It resembles the barium and zinc salt in being very hygroscopic, and exploding easily, when heated with strong sulphuric acid.

*Action of Nitric Acid on Trinitrophenylmalonic Ester.*

The action of nitric acid upon this substance is similar to its action with the bromtrinitrophenylmalonic ester,<sup>1</sup> that is, the nitrite or the substituted tartronic ester is obtained according to the length of the treatment.

*Nitrite of Trinitrophenylmalonic Ester,*  
 $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CONO}(\text{COOC}_2\text{H}_5)_2$ .

Two grams of the trinitrophenylmalonic ester were heated on the steam-bath with about 15 cc. of common strong nitric acid. After three minutes the ester had melted to a clear, red, oily globule, and the entire liquid had taken on a reddish color. If the process was continued for two minutes more, the globule went into solution. The heating should not be continued beyond this point ; in fact, it can be stopped to advantage even as soon as the globule of the melted substance is

<sup>1</sup> This JOURNAL, 14, 336, 345.



formed. If all the organic matter had gone into solution, reddish crystals separated in large quantity, as the liquid cooled. These were purified by washing with water and several crystallizations from alcohol until they showed the constant melting-point  $109^{\circ}$ . The globule, if the process was stopped before it disappeared, was allowed to solidify, and then purified in the same way. The substance was dried *in vacuo* and analyzed with the following result:

0.2190 gram of the substance gave 25.8 cc. of nitrogen, at a temperature of  $20^{\circ}$  and a pressure of 760.8 mm.

	Calculated for $C_6H_2(NO_2)_3CNO_2(COOC_2H_5)_2$ .	Found.
N	13.46	13.46

*Properties of the Nitrite of Trinitrophenylmalonic Ester.*

It crystallizes in long, flat, white prisms, apparently belonging to the monoclinic system, usually terminated by two planes at an obtuse angle to each other, but sometimes only by a single plane. It melts at  $109^{\circ}$  with decomposition, as shown by the appearance of a red color. It is easily soluble in ethyl or methyl alcohol, or in chloroform, ether, benzol, glacial acetic acid, or acetone; nearly insoluble in carbonic disulphide; essentially insoluble in water, when cold, very slightly soluble in hot water, giving a pink solution. The three strong acids have no apparent action with it in the cold; strong sulphuric acid, when hot, decomposes it, as shown by the dark color produced and the evolution of gas; strong nitric acid, when hot, converts it into the corresponding tartronic ester. Alkalies have no action upon it at first, but gradually decompose it in the cold with the formation of a red solution. This action is much hastened by heat, but we have made no attempt to isolate the uninviting product.

In all these respects the nitrite of trinitrophenylmalonic ester resembles the nitrite of bromtrinitrophenylmalonic ester,<sup>1</sup> but we have not succeeded in converting the former into the corresponding tartronic ester by decomposition by heat, as was done with the latter. No crystalline substance could be obtained from the viscous red product of the fusion.

<sup>1</sup> This JOURNAL, 14, 339.

*Trinitrophenyltartronic Ester*,  $C_6H_2(NO_2)_3COH(COOC_2H_5)_2$ .

This substance was obtained by long continued action of hot nitric acid on trinitrophenylmalonic ester, or by the action of the same reagent on the nitrite just described. Two grams of trinitrophenylmalonic ester were warmed in a porcelain dish on the water-bath with about 15 cc. of common strong nitric acid, more acid being added from time to time to take the place of that which evaporated. To secure the complete formation of the tartronic ester, the heating should be continued for five hours. If the acid solution was not too concentrated, it deposited on cooling long needles of a pink color arranged in rosettes. Stronger solutions gave a more or less red solid cake of the same compound. It was purified by washing with water, and two recrystallizations from alcohol by cooling, when it showed the constant melting-point  $117^\circ$ , and after drying *in vacuo* was analyzed with the following results :

I. 0.2129 gram of the substance gave 20.8 cc. of nitrogen at a temperature of  $21^\circ$  and a pressure of 769.7 mm.

II. 0.2051 gram gave 20.3 cc. of nitrogen at a temperature of  $25^\circ$  and a pressure of 750.3 mm.

	Calculated for $C_6H_2(NO_2)_3COH(COOC_2H_5)_2$ .	I.	Found.	II.
N	10.85	11.24		10.87

The analysis of this substance gave much trouble, because of the ease with which it exploded, but the difficulties were overcome by mixing it with a large amount of cupric oxide, and heating very carefully.

*Properties of Trinitrophenyltartronic Ester.*—It forms white, fluffy needles in clusters like sheaves or even circles. Under the microscope the crystals are seen to be slender prisms terminated by a single plane at an oblique angle. Its melting-point is  $117^\circ$ . It is easily soluble in ethyl or methyl alcohol, in fact the hot concentrated solution in ethyl alcohol is so strong that it solidifies nearly completely on cooling. It is also easily soluble in ether, benzol, chloroform, or acetone; soluble in glacial acetic acid; somewhat soluble in carbonic disulphide; soluble with difficulty in ligroin; insoluble in cold water, slightly soluble with decomposition in hot, forming a reddish solution. The three strong acids have no apparent effect

on it in the cold, but hot strong sulphuric acid decomposes it, giving a dark color and an evolution of gas. Alkalies give with it at once dark, blood-red solutions probably containing its salts, but these decompose rapidly, turning dirty-brown, and we have not succeeded in isolating the salts themselves, or any definite compounds from their decomposition-products.

*Trinitrophenylacetyltartronic Ester,*



Acetyl chloride dissolves trinitrophenyltartronic ester easily, but does not react with it either at ordinary temperatures, or when heated on the steam-bath in open vessels. We accordingly proceeded as follows: Three grams of trinitrophenyltartronic ester were heated with 15 to 20 cc. of acetyl chloride in a sealed tube to  $110^\circ$  for five or six hours. Care was taken that the temperature did not go too high, as at  $140^\circ$  a blackish decomposition-product was also formed, which made the purification of the product more difficult. On evaporating off the excess of acetyl chloride white crystals separated, which were purified by crystallization from alcohol until they showed the constant melting-point  $125^\circ$ , when they were dried *in vacuo*, and analyzed with the following result:

0.2201 gram of the substance gave 19.4 cc. of nitrogen at a temperature of  $24^\circ$  and a pressure of 761.6 mm.

	Calculated for $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{COC}_2\text{H}_5\text{O}(\text{COOC}_2\text{H}_5)_2.$	Found.
N	9.79	9.88

*Properties of Trinitrophenylacetyltartronic Ester.*—It forms white, flat, rather broad prisms, or perhaps they should be called tables, terminated by two planes, and apparently belonging to the monoclinic system. It melts at  $125^\circ$ , and is easily soluble in ethyl or methyl alcohol, benzol, chloroform, or acetone; somewhat soluble in ether, less so in carbonic disulphide; soluble in glacial acetic acid; insoluble in ligroin; insoluble in cold water, slightly soluble in hot, forming a pink solution. Strong hydrochloric acid does not dissolve it. Nitric acid when hot dissolves it apparently without decomposition. Sulphuric acid dissolves it, and decomposes it, when heated. Alkalies have no effect on it in the cold, but,

if heated with it, form the red salts of its decomposition-product.

The benzoyl derivative of trinitrophenyltartronic ester was also made, but the close of the academic year prevented us from getting a satisfactory analysis of it. It was made by heating the tartronic ester with benzoyl chloride in a sealed tube to  $110^{\circ}$  for four or five hours. On evaporating off the excess of benzoyl chloride it was obtained in white crystals, which were purified by recrystallization from alcohol until they showed the constant melting-point  $152^{\circ}$ .

*Saponification of Trinitrophenylmalonic Ester.*

In all these experiments the modification melting at  $64^{\circ}$  was used. The method of saponification adopted was that which had given such excellent results with the other substituted malonic esters studied in this laboratory, that is, the action of sulphuric acid diluted to a specific gravity of 1.44. Five grams of trinitrophenylmalonic ester were mixed with 100 cc. of this acid, and the mixture boiled in a flask with a return-condenser. The ester melted almost immediately to a straw-colored oily liquid, which gradually decomposed with evolution of gas, and finally was completely dissolved. This usually took place in from one and a half to two and a half hours, and showed that the reaction had come to an end. During the earlier part of the boiling the liquid appearing in the condenser had a pinkish color, but this disappeared later in the process. As soon as all the ester had dissolved, the liquid was allowed to cool, when it deposited a bulky precipitate made up of yellowish-white needles. This substance consisted of the trinitrophenylacetic acid, and was purified in the way described in the following paragraph.

*Trinitrophenylacetic Acid*,  $C_6H_2(NO_2)_3CH_2COOH$ .—The purification of this substance cannot be effected by crystallization from alcohol or water, as either of these solvents converts it into the corresponding substituted toluol,



We tried at first as a solvent water containing a small amount of sulphuric acid, since this had given excellent results with

bromdinitrophenylacetic acid;<sup>1</sup> but, whereas with that substance a few drops of sulphuric acid were sufficient to prevent the formation of the substituted toluol, we found that even 1 per cent of acid did not produce this effect with the trinitrophenylacetic acid, and that the amount must be raised to 5 per cent to insure perfect safety. Fortunately it was not necessary to use this rather strongly acidified water, as benzol proved to be an excellent solvent for the substance. Accordingly the crystals, which formed the product of the saponification (see the preceding section), were filtered from the sulphuric acid through glass wool, washed with water, dried, and recrystallized from benzol until they showed the constant melting-point  $161^{\circ}$ , when they were dried at  $100^{\circ}$  and analyzed with the following results:

I. 0.2020 gram of the substance gave 28.2 cc. of nitrogen at a temperature of  $22^{\circ}$  and a pressure of 750.8 mm.

II. 0.2093 gram of the substance gave 28.4 cc. of nitrogen at a temperature of  $20^{\circ}$  and a pressure of 758.3 mm.

N	Calculated for $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CH}_2\text{COOH}$ .	I.	Found.	II.
	15.50	15.59		15.46

*Properties of Trinitrophenylacetic Acid.*—It crystallizes from benzol in short needles arranged in sheaf-shaped bunches, and melts at  $161^{\circ}$ . As at first prepared it is white, but it turns pink on standing, even when in a corked tube, and this change is due to decomposition, as it is accompanied by an alteration in the melting-point. It dissolves in ethyl or methyl alcohol with a pink color, but this solution produces a decomposition, the trinitrophenylacetic acid losing carbonic dioxide and forming trinitrotoluol, which is left in a nearly pure state on the evaporation of the solvent. It was recognized by its melting-point,  $81^{\circ}$ . Willbrand<sup>2</sup> gives  $82^{\circ}$ , Mills<sup>3</sup>  $78^{\circ}.84$  and  $80^{\circ}.52$ . (It is possible that further crystallization might have raised the melting-point of our specimen to  $82^{\circ}$ .) The trinitrophenylacetic acid, therefore, is less stable than the bromdinitrophenylacetic acid, as two evaporations with alcohol were necessary to convert this entirely into the corresponding

<sup>1</sup> This JOURNAL, 11, 552.

<sup>2</sup> Ann. Chem. (Liebig), 127, 178.

<sup>3</sup> Phil. Mag. [5], 14, 27.



bromdinitrotoluol. One crystallization of the trinitrophenylacetic acid from boiling water was sufficient also to form the trinitrotoluol, and, as has been already said, the addition of 5 per cent. of sulphuric acid was necessary to prevent this action. The aqueous solution had a pink color like that of the alcoholic solution, but we have not succeeded in discovering the cause of this coloration, which disappears from the solutions, as the substituted toluol is purified by recrystallization. The solvents which follow dissolve the trinitrophenylacetic acid without decomposition; easily soluble in ether, glacial acetic acid, acetone, or ligroin; soluble in chloroform, less so in benzol or carbonic disulphide. The best solvent for it is benzol. The three strong acids seem to dissolve it without decomposition; it is more soluble in nitric acid or sulphuric acid than in hydrochloric acid. Alkalies dissolve it easily, forming deep blood-red solutions of its salts, but we have not yet succeeded in bringing any of these salts into a state fit for analysis.

*Attempts to Make Ditrinitrophenylmalonic Ester.*

Dittrich,<sup>1</sup> in his work on the action of picryl chloride on sodium acetacetic ester, obtained without difficulty a ditrinitrophenylacetacetic ester; in fact this substance occurred as a secondary product in his preparations of trinitrophenylacetacetic ester, when he used the reagents in molecular proportions. It seems strange, therefore, that we have never observed the formation of a ditrinitrophenylmalonic ester as a secondary product in any of our preparations of the monosubstituted ester. In the hope of preparing this substance (ditrinitrophenylmalonic ester) we converted 5 grams of the trinitrophenylmalonic ester into its sodium salt by treatment with the sodic ethylate from 0.31 gram of sodium, and then treated it with 3.4 grams of picryl chloride. The mixture was allowed to stand at ordinary temperatures over night, and, as no apparent change had taken place, it was divided into two portions, one of which was heated on the steam-bath until it turned brown, and the other allowed to stand two weeks, when it had also turned brown, and deposited crystals of sodic

<sup>1</sup> Ber. d. chem. Ges., 23, 2720.



chloride. The brown solutions, whether obtained by heating or by standing, yielded sodic picrate and a brown viscous mass, from which nothing fit for analysis could be isolated. A repetition of the experiment under other conditions gave the same result. It seems, therefore, that picryl chloride brings about a deep-seated decomposition when it acts on the sodium salt of the trinitrophenylmalonic ester, as the ditrinitrophenylmalonic ester would be without doubt a well-crystallized compound. The products of this reaction recall Dittrich's description of the substances obtained by him from the action of picryl chloride on sodium malonic ester (pikrinsaures Natrium neben schmierigen Zersetzungsproducten des Malonsäureesters), and it may be that the presence of an excess of picryl chloride was the cause of his failure to obtain trinitrophenylmalonic ester, although this does not appear from the statement in his paper.

Some experiments on the action of aniline on trinitrophenylbrommalonic ester yielded only viscous unmanageable products; and boiling it with water gave no more promising results.

We have also tried several times to detect the presence of trinitrobenzol in the secondary products of the action of sodium malonic ester on picryl chloride, but without success. It seems, therefore, that the replacement of the chlorine of the picryl chloride by hydrogen does not take place under these conditions to any great extent, if it occurs at all.

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Contributions from the Chemical Laboratory, University of Oregon.

## I.—THE RELATION OF TRIVALENT TO PENTAVALENT NITROGEN.

BY ARTHUR LACHMAN.

[FIRST PAPER.]

### THE ACTION OF ZINC ETHYL ON NITRO- AND NITROSO-COMPOUNDS.

Under the above general title it is proposed to publish, from time to time, a series of more or less connected experimental investigations, their common feature being a study of the

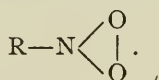
changes of valence of nitrogen atoms. The present paper deals with the structure of the nitro-group,  $-\text{NO}_2$ .

In one form or another, the problem raised by this simple atonic grouping is attracting considerable attention. Without entering into detail, two conditions of the subject may be selected from the great mass of material. In the first place, experimental work has dealt almost wholly with the structure of acidic-nitro compounds and their salts, nitroparaffin salts,<sup>1</sup> isomeric nitroparaffins of the benzyl series,<sup>2</sup> primary nitramines,<sup>3</sup> isonitramines,<sup>4</sup> and primary nitrosamines.<sup>3</sup> These substances are not treated in the present paper, and this brief reference will suffice. In the second place, the structure of the neutral nitro-group is regarded as entirely unsettled,<sup>5</sup> and no experiments have been made to unravel it.

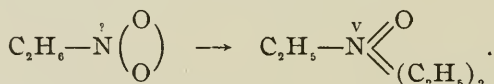
In fact, what little evidence can be adduced in support of one or the other possible formulæ,



is wholly deductive in its character. Spectrochemical calculations have led Brühl<sup>6</sup> to the conclusion that nitroparaffins as well as nitrobenzenes have the same structure; *viz.*,



The same charge of deductive reasoning may be made against the single experimental research dealing with our problem. Bewad,<sup>7</sup> in an attempt to ascertain the structure of nitroethane, found that this substance reacts with zinc ethyl, producing triethylamine oxide. This reaction may be regarded as the replacement of an oxygen atom in nitroethane by its equivalent, two ethyl groups:



<sup>1</sup> Nef: *Ann. Chem. (Liebig)*, **280**, 263.

<sup>2</sup> Hantzsch: *Ber. d. chem. Ges.*, **29**, 699, 2251.

<sup>3</sup> Thiele and Lachman: *Ann. Chem. (Liebig)*, **288**, 271, 280.

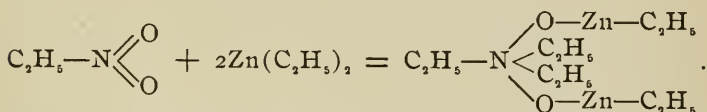
<sup>4</sup> Traube: *Ber. d. chem. Ges.*, **28**, 2297.

<sup>5</sup> Cf. Meyer-Jacobson, *Lehrbuch*, p. 254.

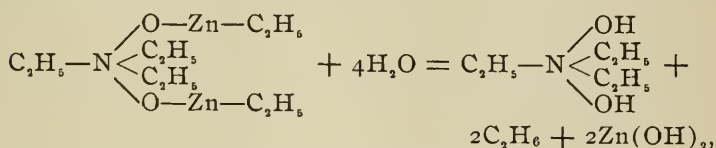
<sup>6</sup> *Ber. d. chem. Ges.*, **31**, 1350.

<sup>7</sup> *Ibid.*, (Ref.), **21**, 479; **22**, 250.

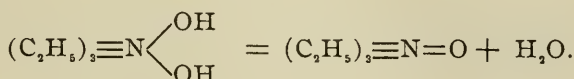
Assuming that zinc ethyl acts on nitrogen-oxygen compounds as it does on the carbonyl group, Bewad interpreted the mechanism of this reaction as follows: In the first place addition of two molecules of zinc ethyl occurs :



Reacting with water in the usual manner, this addition-product forms dihydroxytriethylamine :

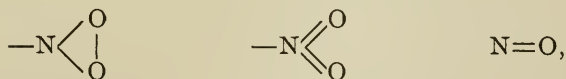


which finally loses water, triethylamine oxide being the result :



For lack of other evidence, the interpretation seems plausible enough. It is strange, however, that Bewad recommends the use of but one molecule of zinc ethyl ; the employment of two led him to an entirely different substance, whose constitution he did not determine.

The question which Bewad's interpretation raises, however, suggests a possible mode of approach. If we compare the two structures under question with the constitution of the nitroso-group,



we see that a doubly linked oxygen atom occurs in the latter and in one of the former. If, therefore, the nitro-group contains oxygen atoms in this form, we may reasonably expect to find nitroso-reactions duplicated, to a greater or less extent, in the corresponding reactions of nitro-compounds. Conversely, marked differences in such reactions would lead us to the opposite conclusion.

From this point of view, various nitroso- and nitro-compounds have been subjected to the action of zinc ethyl. Two prefatory explanations are in order. In the first place, but one representative of the numerous subgroups has been examined. This limitation was imposed by the few facilities at my command, and by the necessity of a general, though incomplete, survey of the field as a whole. In the second place, the results here recorded apply only to a laboratory temperature whose average is  $10^{\circ}$ , and whose maximum does not exceed  $15^{\circ}$ . On warming the various substances with zinc ethyl, the reactions assume a complicated character which greatly increases the difficulties of the work, and above all renders comparisons impossible. The results of the reactions at higher temperatures are interesting in themselves, however, and they will be reported at some later date.

*Theoretical Part.*

Three nitrosamines were examined. Diethylnitrosamine,  $(C_2H_5)_2N-NO$ , purely aliphatic, and phenylmethylnitrosamine,

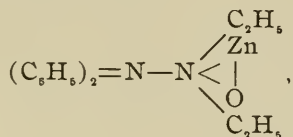
amine,  $\begin{array}{c} CH_3 \\ \diagup \\ C_6H_5 \end{array} N-NO$ , semiaromatic, do not react with zinc

ethyl. Diphenylnitrosamine,  $(C_6H_5)_2N-NO$ , reacts with violence, so that the substances must be brought together in dilute solution. We may reasonably conclude that increasing negativity of the molecule as a whole enables the nitroso-group to react with zinc ethyl.

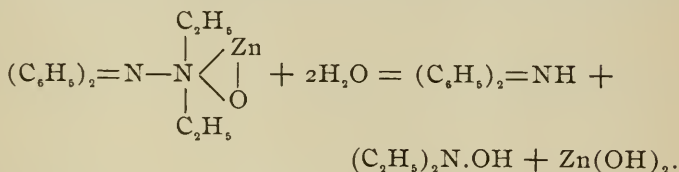
The nature of this reaction is novel and unparalleled. There is formed a well-characterized addition-product, consisting of one molecule each of zinc ethyl and diphenylnitrosamine. This addition-product is decomposed by water, without evolution of gas; the products are zinc hydroxide, diphenylamine, and a volatile base. As the theoretical quantity of diphenylamine is obtained, diphenylnitrosamine reacts completely with zinc ethyl—a condition which has not been observed in the case of any of the other nitrogen compounds investigated. The volatile base at first occasioned much trouble, owing to the impossibility of obtaining it or its salts in a pure state; but as it is a strong reducing-agent, and is converted by reduction into diethylamine, it can be nothing but  $\beta\beta$ -diethyl-

hydroxylamine.<sup>1</sup> Nearly 50 per cent of the theoretical quantity of diethylamine was isolated.

The constitution of the addition-product is thus fully explained by the following formula :



which satisfactorily accounts for its decomposition by water :



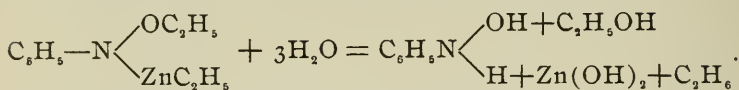
I know of no other instance in which zinc ethyl thus parts with both alkyls at once to a single other atom. If this unexpected reaction is to be explained by the affinity of nitrogen for alkyl, it is inconceivable why the much more basic diethylnitrosamine does not manifest the same activity. If, on the other hand, it is due to the general negativity of the molecule, it is equally strange that nitrosobenzene does not behave similarly (see next paragraph).

Among compounds containing the nitroso-group directly attached to carbon, but one could be investigated. This was nitrosobenzene. The reaction between nitrosobenzene and zinc ethyl is far from simple,<sup>2</sup> and it will be impossible to give any equation representing it. The salient features are the violence of the reaction, which takes place immediately even in dilute solution, with evolution of much heat ; the formation of azoxybenzene as chief product, and of phenylhydroxylamine in almost equal quantity ; the production of smaller amounts of aniline and ethylaniline ; and the total absence of diethylaniline. The formation of azoxybenzene is of course easily accounted for by the interaction of nitrosobenzene with

<sup>1</sup> An attempt will be made to prepare this base in quantity by this curious synthesis.

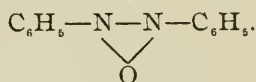
<sup>2</sup> Cf. with the reaction between nitrosobenzene and diazomethane (Von Pechmann: Ber. d. chem. Ges., 30, 2461). There are many points of similarity.

phenylhydroxylamine.<sup>1</sup> As to this latter substance, the following equation may be offered (with reservation) :

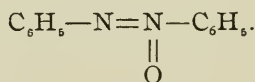


No simple equations can be suggested that will explain the appearance of aniline and ethylaniline. A considerable quantity of neutral, black tar is a constant product ; its properties are uninviting, but further investigation of it may lead to a more complete explanation of this complex reaction.

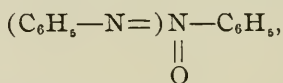
As intermediate between the two groups of compounds just considered, the behavior of azoxybenzene towards zinc ethyl offered an interesting problem. The constitution of this substance is commonly given thus :



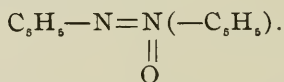
This formula, however, rests upon absolutely no experimental basis ; and an alternative structure is frequently offered :<sup>2</sup>



Brühl, indeed, has declared that the latter formula<sup>3</sup> alone can be regarded as consistent with the spectrochemical equivalent of the substance. The Brühl formula may be regarded as representing either a modified nitrosobenzene,



or a modified diphenylnitrosamine,



<sup>1</sup> Bamberger : Ber. d. chem. Ges., 30, 2280.

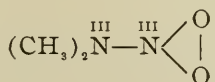
<sup>2</sup> Meyer-Jacobson, II, p. 251.

<sup>3</sup> Ber. d. chem. Ges., 31, 1361. The third possibility mentioned by Brühl,  $\text{C}_6\text{H}_5-\text{N}=\text{N}(\text{O})-\text{C}_6\text{H}_5$ , offers but little attraction from the purely chemical point of view.



The resemblance to the latter substance seems the closer, by the fact that diphenylnitrosamine and azoxybenzene are isomeric. A substance with the Brühl formula ought, therefore, to react easily and promptly with zinc ethyl. Experiment showed, however, that azoxybenzene does not react with zinc ethyl even on standing fourteen days. Azoxybenzene thus has the structure usually assigned to it. A further conclusion may be drawn from this result—an oxygen atom linked to two other atoms is not readily attacked by zinc ethyl—a conclusion of value in connection with one of the possible structures of the nitro-group.

Three nitro-compounds were studied—dimethylnitramine, nitroethane, and nitrobenzene. Dimethylnitramine,  $(\text{CH}_3)_2\text{N}-\text{NO}_2$ , does not react with zinc ethyl. Unfortunately, no binding conclusion can be drawn from this result, since the corresponding nitroso-compound (diethylnitrosamine) exhibits no greater tendency to react. In view of the conclusion reached further on concerning the other two compounds, however, the conjecture may be hazarded that both nitrogen atoms are trivalent :



As regards the conduct of nitroethane, Bewad's<sup>1</sup> results can be almost wholly verified. The amount of triethylamine oxide produced is about 12 per cent of the theoretical yield ; no attempt has been made for the present to ascertain the cause of the great loss. At variance with Bewad, however, I found that the presence of two molecules of zinc ethyl does not prevent the appearance of triethylamine oxide ; on the contrary, the yield was increased to 25 per cent. The cause of this discrepancy can only be surmised.<sup>2</sup>

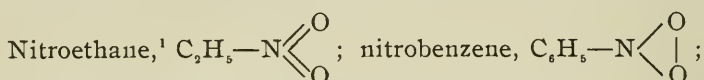
Nitrobenzene proves a great surprise, for it reacts but slightly with zinc ethyl. Nearly fifty per cent is recovered unaltered, and the bulk of the reaction-product is a neutral, sticky mass of disagreeable character. The small amount of

<sup>1</sup> *Loc. cit.*

<sup>2</sup> On allowing a mixture of equal molecules of the substances to stand forty-five days, hardly any oxide was obtained. Perhaps Bewad allowed his solution to stand too long.

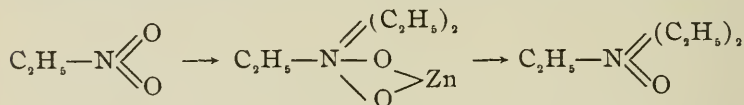
basic matter obtained consists chiefly of hydroxylamine, with traces of aniline and monoethylaniline; no diethylaniline could be found. Similar results were obtained when two molecules of zinc ethyl were allowed to act on nitrobenzene, except that 4 per cent ethylaniline was found in this case.

Taking into consideration the general result reached with nitroso-compounds, *viz.*, that negativity and reactivity are proportional, the conclusion seems inevitable that nitrobenzene and nitroethane are differently constituted. As nitroethane is more reactive, taking up two ethyl groups where nitrobenzene barely takes up one; as nitrobenzene closely approaches azoxybenzene in its behavior towards zinc ethyl; and as nitrosobenzene acts violently under similar circumstances, we arrive concordantly at the general conclusion that nitroparaffins and nitroaromatics belong in different categories, thus:



and that the "spectro-chemistry of nitrogen" is not a safe guide for the present.

As to the mechanism of Bewad's reaction, nothing definite can be postulated. Zinc ethyl is undoubtedly capable of exchanging both its alkyls for a single oxygen atom, as in the case of diphenylnitrosamine. If it were possible to isolate the intermediate product which nitroethane<sup>2</sup> must form, the question might easily be settled, but the experimental difficulties preclude this for the time being. Perhaps it is as well to abide by what evidence we have in the nitrogen-oxygen group, and replace Bewad's interpretation by the following:



An attempt will be made to verify this hypothesis at some subsequent opportunity.

<sup>1</sup> This nitroparaffin formula agrees much better with Nef's conception of their salts,  $\text{CH}_3\text{CH}=\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OMe} \end{array}$ , than with Hantzsch's:  $\text{CH}_3\text{CH}=\text{N}-\text{OMe}$ .

<sup>2</sup> Bewad describes one of exceedingly complex composition.

The regular gradation of properties which has facilitated the study of so many series of organic compounds, and which has contributed so largely to the rapid growth of the science, is lacking in the groups under consideration. As in the tautomerism of ketones,<sup>1</sup> as in the behavior of acid amides,<sup>2</sup> so in the more intimate chemistry of nitrogen each substance is a law unto itself, and we know not to-day what the morrow may bring forth.

### Experimental Part.

*Diethylnitrosamine*.—1.5 grams stood with 1.5 grams zinc ethyl for twenty-four days. It was recovered unaltered, and no other products could be found.

*Phenylmethylnitrosamine*.—9 grams each of this substance and zinc ethyl stood fourteen days in solution in benzene; on pouring into water there was violent reaction. 8.8 grams nitrosamine were recovered; the acidified aqueous solution contained traces of aromatic bases.

*Diphenylnitrosamine*.—The following experiment is typical: 4 grams zinc ethyl were mixed with 100 cc. benzene (sodium dried), and 6 grams nitrosamine added at one time. In a few minutes violent ebullition took place, and continued for a short while. A portion of the solution was then carefully evaporated in the cold in a current of dry carbon dioxide; a gelatinous paste remained, which when rubbed on a porous plate, solidified to a dry, yellow powder. In subsequent experiments the solution was worked up directly.

The solid addition-product shrivels between 135°–140°, is stable in dry air, and insoluble in ordinary solvents. Water and alcohol decompose it without evolution of gas.

0.2414 gram gave 0.0626 gram zinc oxide upon ignition.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> N.NO.Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> .	Found.
Zn	20.8	20.3

Ten grams nitrosamine and 6 grams zinc ethyl, after reaction, were treated with just enough dilute sulphuric acid to dissolve the precipitated zinc hydrate. The benzene solution, after drying, left 8.3 grams diphenylamine (calculated

<sup>1</sup> Cf. Claisen: *Ann. Chem. (Liebig)*, **291**, 45.

<sup>2</sup> Cf. Lachman: *This JOURNAL*, **18**, 600.

8.4 grams). The substance was identified by its melting-point,  $54^{\circ}$ , its boiling-point (the whole quantity distilled unchanged at  $304^{\circ}$  and 758 mm.), and by the "diphenylamine reaction."

The aqueous acid solution reduces Fehling's solution in the cold; on rendering alkaline and distilling in steam, the reducing base passes over; on neutralizing with hydrochloric acid and evaporating, ethyl chloride is given off, and but a small quantity of solid is left which gives no satisfactory results on analysis.<sup>1</sup>

The volatile base was determined by reduction to diethylamine.<sup>2</sup> 16 grams nitrosamine and 10 grams zinc ethyl were worked up as above; the acid solution was mixed with an equal volume of glacial acetic acid, and zinc dust added in small quantities until the solution no longer reduced Fehling's solution. The mixture was then filtered, made alkaline, and distilled with steam, the distillate neutralized with hydrochloric acid, evaporated to dryness, and extracted with cold alcohol. There remained 1.2 grams ammonium chloride (does not melt, nor react with nitrous acid, gives no isonitril); the alcohol left 4.3 grams diethylamine hydrochlorate on evaporation (calculated 8.8 grams). It was identified thus: conversion into the nitrosamine gave 2.5 grams boiling at  $174^{\circ}$ – $175^{\circ}$  (corr.); calculated 3.4 grams. The nitrosamine was reconverted into the hydrochlorate, and the salt finally analyzed:

0.1753 gram required 15.95 cc. (corr.) silver nitrate solution (1 cc. = 0.01088 gram Ag) for complete precipitation according to Volhard.

	Calculated for (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH.HCl.	Found.
Cl	32.4	32.5

*Nitrosobenzene*.—The reactions were carried out in the following manner: The zinc ethyl was diluted with about four times its volume of benzene, and a saturated solution of nitrosobenzene in the same solvent added slowly, constantly cool-

<sup>1</sup> Cf. the similar experiences of Gürke, Ann. Chem. (Liebig), 205, 274, and of Kjellin, Ber. d. chem. Ges., 30, 1893.

<sup>2</sup> Diethylamine is not present before reduction; the solution from 16 grams nitrosamine gave no diethylnitrosamine with sodium nitrite.

ing with very cold tap water. The characteristic green color of nitrosobenzene disappears at once, but the mixture was allowed to stand several hours before working up. A considerable excess of zinc ethyl was usually taken, to insure complete reaction of the nitrosobenzene. No gas is given off on mixing the solutions. The method of procedure was simple. The benzene solution was slowly added to the calculated quantity of dilute sulphuric acid (2N), with constant cooling; after thorough shaking, each layer was filtered to remove traces of the other, and the benzene solution dried over calcium chloride.

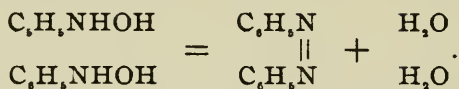
*a. Contents of the Benzene Solution.*—After evaporation, cold ligroin extracts almost pure azoxybenzene (melting-point  $28^{\circ}$ , after one crystallization,  $35^{\circ}$ – $36^{\circ}$ ), which is obtained in the characteristic pale-yellow needles. A dark tarry substance remains, which was not examined further. The quantity of azoxybenzene is comparatively large; thus, 10.5 grams nitrosobenzene and 15 grams zinc ethyl gave 4.7 grams neutral residue, from which ligroin extracted 2.6 grams azoxybenzene. Recalculated as nitrosobenzene, this amounts to 25 per cent of the total. Regarding the tar as polymerized nitrosobenzene,<sup>1</sup> we can account for an additional 20 per cent.

*b. Contents of the Acid Solution.*—This contains phenylhydroxylamine, small quantities of aniline and ethylaniline, and traces of other substances. No diethylaniline was found at any time. The presence of phenylhydroxylamine was shown by its reactions; the solution when warmed with potassium bichromate or ferric chloride gave the characteristic odor of nitrosobenzene, green globules forming on the sides of the test-tube. The solution also reduces ammoniacal silver at once. An indication of its quantity is given by the following facts: The acid solution from the above experiment (in which azoxybenzene was determined), was rendered weakly alkaline and distilled with steam. Volatile bases passed over, along with a red, neutral substance. By extracting the acidified distillate with ether, 1.85 grams of a red solid were obtained, which melted at  $58^{\circ}$ ; it was purified by distilling in a test-tube, when it melted at  $65^{\circ}$ – $66^{\circ}$ . The substance was therefore

<sup>1</sup> Ber. d. chem. Ges., 31, 1513.



azobenzene,<sup>1</sup> which was probably formed according to the process described by Bamberger:<sup>2</sup>



On the basis of this reaction there would seem to have been present 2.25 grams phenylhydroxylamine, equivalent to a minimum of 21 per cent of the original nitrosobenzene.

The accompanying volatile bases were accidentally lost; to determine their character, 12 grams nitrosobenzene and 20 grams zinc ethyl (large excess) were worked up. 3.5 grams dry base were obtained. 1.7 grams were dissolved in dilute hydrochloric acid and diazotized at 0°. The solution was extracted at once with ether,<sup>3</sup> the liquids quickly separated, and the ether washed with caustic soda, dried, and evaporated. 1.4 grams dark-yellow oil were obtained, which gave Liebermann's reaction with phenol and concentrated sulphuric acid; it solidifies on cooling, and melts again at about 12°. This corresponds to 2.4 grams total ethylaniline, a yield of 14 per cent (calculated 16.8 grams). After extracting the nitrosamine, the diazotized solution was made alkaline and again extracted with ether; the ether contained mere traces of a red substance. A blank test showed that less than 0.1 gram dimethylaniline can be identified by this reaction. Diethylaniline was therefore absent. The aniline still present in the alkaline solution (as diazobenzene) was not estimated (its presence was shown with  $\beta$ -naphthol); by difference it is found to be 1.1 grams.

Computing the various substances obtained in this reaction in terms of nitrosobenzene, a total of 92 per cent is found as a minimum, without taking account of inevitable losses in

<sup>1</sup> On one occasion azoxybenzene appeared at this stage.

<sup>2</sup> Ber. d. chem. Ges., 27, 1550.

<sup>3</sup> The following simple device may be recommended when a freezing-mixture is not at hand: The acid solution is covered with a layer of ether in a filtering-flask, and a current of air forced through both liquids. The temperature rapidly sinks below 0°. A solution of sodium nitrite is then slowly added. The nitrosamine thus comes into immediate contact with ether, and is at once removed from further action without risk of loss or rise in temperature.

<sup>4</sup> This melting-point is approximate; the nitrosamine of methylaniline melts at 17°.



manipulation. This in itself is a sufficient guarantee that nothing of importance has been overlooked.

*Azoxybenzene*.—2 grams were allowed to stand in solution in benzene with 3.5 grams zinc ethyl. After fourteen days, 1.8 grams were recovered.<sup>1</sup> Azoxybenzene is one of the substances which gave an interesting reaction on warming with zinc ethyl; details will be published later.

*Dimethylnitramine*.—3.5 grams stood nineteen days in ether solution with 5 grams zinc ethyl. On pouring into ice-cold dilute sulphuric acid, and extracting six times with ether, 3.4 grams were recovered.

*Nitroethane*.—At first Bewad's<sup>2</sup> directions were followed; a modification which is more expeditious will be described later. 24 grams nitroethane and 46 grams zinc ethyl were allowed to stand sixteen days in ether solution. 3.1 grams triethylamine oxide were obtained as a perfectly colorless oil boiling between 157°–158° (753 mm.) without decomposition.<sup>3</sup> Calculated for 24 grams nitroethane, 39 grams. However, 7 grams nitroethane were recovered, making a total yield of 12 per cent triethylamine oxide.

Bewad's results with 2 molecules of zinc ethyl were not confirmed. 20 grams nitroethane and 63 grams zinc ethyl stood in 100 cc. ether for fourteen days. 7 grams triethylamine oxide were obtained (25 per cent of the calculated yield). The neutral residue contained about 2 grams nitroethane; Bewad's substance boiling at 178°–180° could not be found.

*Nitrobenzene*.—9 grams each nitrobenzene and zinc ethyl stood in solution in ether for fifteen days. Practically no gas was evolved on pouring into ice-cold dilute sulphuric acid. The acid solution was treated as in the case of nitrosobenzene. A small amount of phenylhydroxylamine was found, (quantity not accurately determined: estimated at 0.5 gram), and mere traces of aniline and ethylaniline; no diethylaniline was present. The neutral ether solution left a dark oil, which was distilled with steam; the distillate was collected in ether and fractioned; 4.5 grams nitrosobenzene (boiling-point 210°–

<sup>1</sup> This slight deficit was caused by the occasional removal of a small quantity to note the progress of the reaction.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> The properties of triethylamine oxide will form the subject of a separate communication.

215°) were recovered,<sup>1</sup> amounting to 50 per cent of the original material. The residue weighed 3.4 grams, forming a dark-red, sticky mass, which did not solidify at -20°; nothing tangible could be extracted from it.

Practically identical results were obtained from the use of 2 molecules of zinc ethyl. 7 grams nitrobenzene stood with 14 grams zinc ethyl as above. There were obtained 0.35 gram ethylphenylnitrosamine (equivalent to 4 per cent of the theoretical quantity of ethylaniline), 3.5 grams nitrobenzene, and 2.7 grams non-volatile tarry residue.

*The Preparation of Zinc Ethyl.*—The large quantities of zinc ethyl needed for the above experiments were manufactured according to the modified Gladstone-Tribe process described by me some time ago.<sup>2</sup> The following additional data will demonstrate the advantages of this method as to convenience and yield. 650 grams ethyl iodide were worked up in seven successive portions. 201 grams redistilled zinc ethyl of constant boiling-point were obtained, with about 15 grams material boiling at a lower temperature; calculated yield 256 grams. Time, five hours. 300 grams ethyl iodide were employed in a single operation; yield, 92 grams redistilled zinc ethyl and 3 grams lower-boiling products (calculated, 108 grams). Time, one hundred and ten minutes.

EUGENE, OREGON, March, 1899.

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## REVIEWS AND REPORTS.

### *Gases of the Atmosphere.*

The German Chemical Society, from time to time, invites chemists who are engaged in work on special lines in which they are recognized as authorities, to lecture before the Society upon their specialties. Among those who have been thus honored are Victor Meyer,<sup>3</sup> who lectured on Stereochemistry; Emil Fischer,<sup>4</sup> on Syntheses in the Sugar Group; O. Wallach,<sup>5</sup> on Terpenes and Camphor; Lothar Meyer,<sup>6</sup> on Inorganic Chemistry According to the Periodic System of the Elements; J. H. van't Hoff,<sup>7</sup> on Theory of Solutions; R.

<sup>1</sup> And about 0.5 gram higher boiling oily residue.

<sup>2</sup> This JOURNAL, 19, 410.

<sup>3</sup> Ber. d. chem. Ges., 23, 567.

<sup>4</sup> Ibid., 23, 2114.

<sup>5</sup> Ibid., 24, 1525.

<sup>6</sup> Ibid., 26, 1230.

<sup>7</sup> Ibid., 27, 6.

Fittig,<sup>1</sup> on Unsaturated Acids; Th. Curtius,<sup>2</sup> on Hydrazines and Triazoic Acid; Robt. Hasenclever,<sup>3</sup> on the Development of the Soda Industry in the past Twenty-five Years; Cl. Winkler,<sup>4</sup> on The Discovery of New Elements; M. Maercker,<sup>5</sup> on Agricultural Chemistry; W. Nernst,<sup>6</sup> on Electrolytic Decompositions of Water Solutions; H. Bunte,<sup>7</sup> on Illumination; and M. Delbrück,<sup>8</sup> on Fermentation. Professor Wm. Ramsay,<sup>9</sup> in response to an invitation from the Society, delivered a lecture in this series on Dec. 19, 1898, upon a subject with which his name will ever be associated, that of "The Newly Discovered Gases and Their Relation to the Periodic System." The lecture was illustrated by photographic projections of the apparatus and exhibitions of the spectra of the gases. While in Berlin, Professor Ramsay gave a private lecture before the Emperor and his family, and also delivered a public lecture upon the same subject. A number of interesting points, which have probably not before been mentioned, were brought out in this lecture before the Society. Prof. Ramsay called attention to the fact that the present arrangement of the periodic system will not accommodate the element argon, with an atomic weight of 40, which should follow potassium; but the fact that the element with higher atomic weight comes first need not destroy our faith in the general arrangement of the system, for the recent work on tellurium has shown its atomic weight to be 127.6, although it precedes iodine with an atomic weight of 126. If the atomic weight of helium is 4 and that of argon 40, there should be, if the usual relation exists between the members of the series, an element with an atomic weight about 16 greater than helium and 20 less than argon. This can be seen from the following arrangement:

H — 1					
Li — 7	Be — 9.2	B — 11	C — 12	N — 14	O — 16
Na — 23	Mg — 24	Al — 27	Si — 28	P — 31	S — 32
			He — 4		
		F — 19	(?) — 20		
		Cl — 35.4	A — 40		

The apparently hopeless task which Prof. Ramsay undertook was to find this missing element, and it is to such an incentive and the work it led to that we owe the discovery of krypton, neon, metargon, and xenon. As suggested

<sup>1</sup> Ber. d. chem. Ges., 27, 2658.

<sup>2</sup> *Ibid.*, 29, 759.

<sup>3</sup> *Ibid.*, 29, 2861.

<sup>4</sup> *Ibid.*, 31, 6.

<sup>5</sup> *Ibid.*, 31, 464.

<sup>6</sup> *Ibid.*, 31, 1547.

<sup>7</sup> *Ibid.*, 31, 5.

<sup>8</sup> *Ibid.*, 31, 1913.

<sup>9</sup> *Ibid.*, 31, 3111.

by the occurrence of helium, all known minerals were tested, but without result. The nitrogen absorbed by magnesium and the ammonia formed from it were thoroughly studied with similar negative results. All attempts to separate substances from argon by diffusion also failed. Although these negative results can be so briefly mentioned they could only be determined by an immense amount of work requiring many months and the greatest skill. When nearly all the possible methods had been tried Ramsay conceived the idea of applying the method of fractional evaporation to the liquefied argon. The argon was liquefied by the use of liquid air, and when most of this air had evaporated it seemed, he said, a pity not to examine the residue. It was the investigation of this which led to the discovery of krypton,<sup>1</sup> the method of isolation and properties of which have already been described. This proved to be the missing element with the atomic weight 22. As also described in the previous note,<sup>1</sup> neon and metargon were found in the fractions from the liquid argon. The neon was always mixed with helium and argon and, as their solubility in ordinary solvents was very slight, they were dissolved in liquid oxygen. By fractional evaporation and removal of the oxygen the neon was obtained in pure condition. To give some idea of the skill and care required for this work, it will only be necessary to give the quantities used to determine the physical constants. The volume of the gas at a pressure of 250 mm. was 30 cc., and the weight of this was 0.0095 gram. An investigation showed that the small amount of these gases present in the argon had no effect on its properties, as the densities of the impure and purified material were 19.94 and 19.96, respectively. They were unable to detect, by the methods available, the presence of xenon by examining 15 liters of argon.

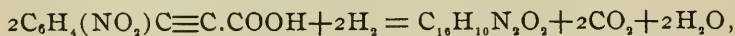
J. ELLIOTT GILPIN.

### *Artificial Indigo.*

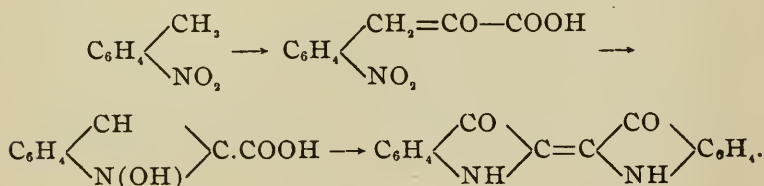
During the past twenty years scientific and commercial circles have been disturbed by periodical reports of the results which it was predicted would follow the discovery of a practical synthetical method for the preparation of indigo, a discovery which would cause serious injury to the vast interests engaged in the preparation of the natural product. Just as the threatened overthrow of the kelp industry by the improved methods of extracting iodine from Chili salpeter, led to the introduction of modern scientific methods in place of those which had been used for years; so the conditions in the indigo industry adjusted themselves to circumstances and the

<sup>1</sup> This JOURNAL, 20, 696.

natural product continued to hold its own. Since the introduction, early in the eighties, of artificial indigo, each step in the improvement and reduction in the price of this article has been met by a similar change in the natural product. This has been due mainly to two causes, an improvement in the methods of obtaining the crude material, and the introduction of cheaper methods of transportation. A method which threatened to affect the industry to a marked degree, was rendered unprofitable by the application of scientific methods in the extraction of the crude dye-stuff and a study of the exact conditions of fermentation, which made it possible to increase the yield to a remarkable degree. By such methods the price of indigo has been greatly reduced, and we are now in one of those periods when it seems as if the time had at last arrived when the natural product can no longer shut out the artificial product, but will be forced to divide the field with it. In the case of all the older methods for the preparation of indigo the difficulties to be overcome have been the cost of the substance from which the indigo is made and the small yield of the dye-stuff. Let us review briefly the history of the production of artificial indigo. Von Baeyer discovered several methods for the preparation of indigo, the most important being the method in which *o*-nitrophenylpropiolic acid is treated with a reducing agent, forming indigo, carbon dioxide, and water, according to the following equation:



and the one in which *o*-nitrobenzoic aldehyde in acetone is treated with alkalis. In 1897 Reissert<sup>1</sup> found that *o*-nitrotoluene with the ester of oxalic acid would form *o*-nitrophenylpyrrolic acid, and that the latter by reduction passed to *N*-oxindolcarbonic acid which can readily be converted into indigo. These changes can be graphically represented as follows:



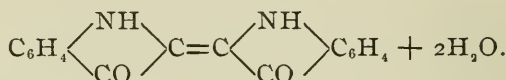
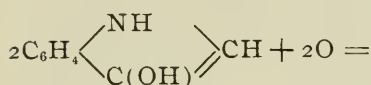
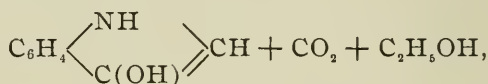
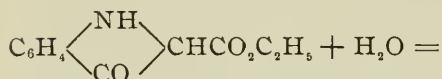
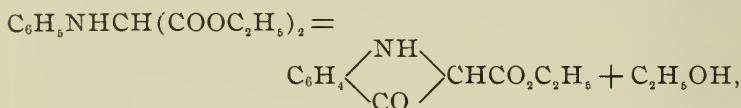
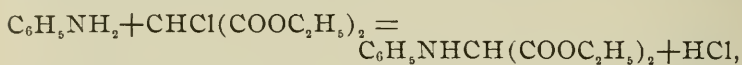
In another method discovered by Blank<sup>2</sup> a few months ago, the indoxyl ester which Von Baeyer had shown could easily be converted into indigo, was prepared by starting with aro-

<sup>1</sup> Ber. d. chem. Ges., 30, 1030.

<sup>2</sup> *Ibid.*, 31, 1812.

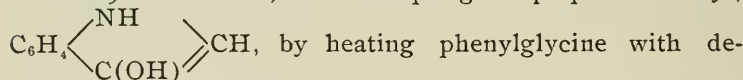


matic amines and esters of chlormalonic acid. From these was obtained an aliphatic aminomalonic acid ester, which by loss of alcohol forms the indoxyl acid ester :

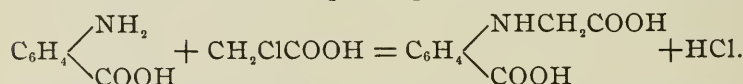


Just what results these methods will give so far as the production on the large scale is concerned cannot yet be determined ; but in the meantime the Badische Anilin- und Soda. fabrik<sup>1</sup> have introduced a synthetical indigo under the name "Indigo rein," which is being manufactured in large quantities, and sold at a price which enables it to compete with the natural product.

In 1890 Heumann,<sup>2</sup> in attempting to prepare indoxyl,



hydrating agents, used sodium hydroxide, and obtained a yellow liquid which, on exposure to the air, gave indigo. In order to prevent the formation of isomers of indoxyl he later used anthranilic acid and obtained by treating this with chloracetic acid, phenylglycine-*o*-carbonic acid :



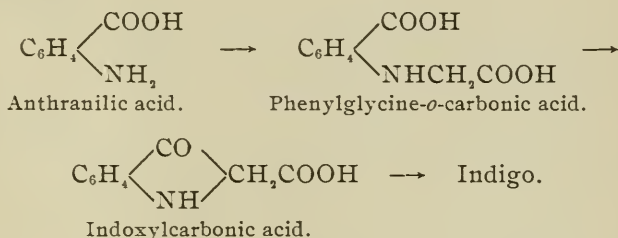
The method finally adopted for transforming this compound into indigo was to heat to 200° with an alkali, dissolve in

<sup>1</sup> Chem. Centralblatt, 1891, I, 560 ; II, 144.

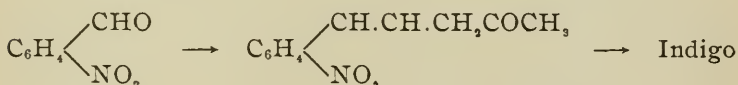
<sup>2</sup> Ber. d. chem. Ges., 23, 3043 ; 23, 3431.



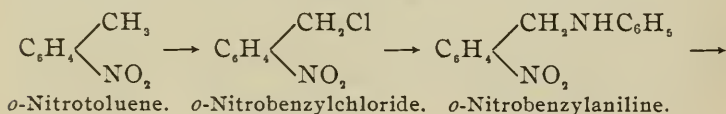
water, and oxidize by forcing air through the solution. It is this method which, according to the best information available, is used by the Badische Anilin- und Sodafabrik for manufacturing the "Indigo rein." The changes can be represented thus :



The transformation of anthranilic acid into indigo can be quite readily and economically carried out, but as the anthranilic acid is obtained from phthalic acid and that in turn from naphthalene, the price at which the indigo can be put on the market depends to a great extent on the relative price of these products. The Badische Anilin- und Sodafabrik<sup>1</sup> have recently patented a process for obtaining phthalic acid from naphthalene by heating with sulphuric acid to 200°. Under these conditions the acid acts as an oxidizing agent, and although the price of the acid has been lowered by this method, perhaps cheaper methods may be discovered for preparing the anthranilic acid. In an address<sup>2</sup> delivered before a Section of the International Congress of Applied Chemistry last July, Prof. P. Friedlaender suggested the possibility of using a method discovered by Von Baeyer and Drewsen. The starting-point is *o*-nitrobenzoic aldehyde, which is converted into *o*-nitrophenyllactic acid ketone, and this in turn into indigo :

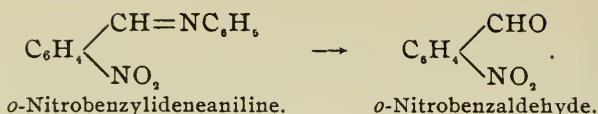


This cannot be a commercially successful process unless the price of the *o*-nitrobenzoic aldehyde is reduced, and this may be possible as patents have recently been taken out for its preparation from *o*-nitrotoluene :



<sup>1</sup> Chem. Ztg., 1897, 21, 291.

<sup>2</sup> *Ibid.*, 1898, 22, 622.



The fact of its preparation and introduction in competition with the natural product raises a number of questions as to the relative value of the two products and their use under different conditions and with different materials.

Natural indigo contains the following constituents: Indigo blue 29-30 per cent, indigo red 2-10 per cent, indigo brown 1-6 per cent, indigo gelatin 2-5 per cent, ash 3-20 percent, and water 3-6 per cent. The artificial indigo contains 97 per cent of indigo blue, the rest consisting of salts and water. It contains no indigo red or indigo gelatin. As to the relative effect of the presence or absence of these constituents there is a great diversity of opinion.

Sigismund Lang,<sup>1</sup> from his observations as a chemist connected with one of the European factories and as Indigo Commissioner, considers the indigo red a necessary ingredient to facilitate the fixing of the dye. He says the dyer values his indigo according to the relative amount of indigo red, the amount desired varying according to the material to be dyed. He ascribes the poor quality of the Java indigo to the small proportion of indigo red present. As the Java indigo is useless from this cause, he therefore argues that "Indigo rein" will be likewise, from the same cause. He acknowledges that the artificial product dyes rapidly, but claims it is not a fast color, and points to the fact that the manufacturers recognize the absence of fixing material in the artificial product as they recommend the use of Turkey-red oil as a fixing agent. Indigo gelatin plays very much the same rôle as the indigo red, but to a less degree.

Carl Bucher,<sup>2</sup> on the other hand, claims that the rôle of the indigo red has been greatly overestimated. It mainly affects the shade of the dye. The indigo white permeates the substance, and is there changed to indigo blue, but the indigo red does not permeate the material to the same degree as the indigo white. The rôle which the indigo gelatin plays can be better taken by the Turkey-red oil, as it causes the rapid absorption of the dye-stuff by the material. The presence of one of these fixing-agents is necessary in dyeing cotton; but not only are they not necessary in the case of wool, but they may be objectionable, and for such work the introduction of this pure substance may prove of great value,

<sup>1</sup> Chem. Ztg., 1897, 21, 961.

<sup>2</sup> *Ibid.*, 1897, 21, 1005.

as its action can be regulated, and results obtained with it which could not be obtained with the impure mixture of the natural product. The field from which the natural indigo has been driven by other dye-stuffs may now be reclaimed by the pure indigo.

An investigation by Binz and Rung<sup>1</sup> showed that 87.89 per cent of the dye-stuff was fixed on the fabric. The artificial product comes in two forms, as a paste and as a powder. It saves all labor of grinding, and the dyeing process can be easily controlled and regulated. It has proved very successful in calico printing; the stamping is clear, and the change into isatin takes place readily. It is now used for making indigo extract and carmine, and the process of testing and valuing is greatly simplified. In 1897 the price of the natural indigo, calculated per kilogram of indigotin, was 12.50-16.50 marks, depending upon the quality, while the artificial was worth 17 marks. The present price of the latter is 16 marks.

An unbiased investigator, after studying the arguments for and against this substance, cannot fail to be impressed with the idea that it has an important rôle to play, and that while it will probably never entirely drive out the natural product yet it will be found more useful for certain purposes than that product, even though it may be more expensive.

J. ELLIOTT GILPIN.

### *Fermentation without Cells.*

In a note in Vol. 20 of this JOURNAL, page 699, an abstract of Edward Buchner's work is given under the above title. The conclusions reached were that alcoholic fermentation is possible without cells, and that fermentation is probably caused by an enzyme which is dissolved in the liquid within the cell of the living yeast, and can be obtained, mixed with other substances, by crushing the cells and expressing the liquid contents.

In Sept., 1898, H. Abeles,<sup>2</sup> of Vienna, opposed Buchner's enzyme theory, offering instead what may be called the plasma hypothesis. Abeles thinks that the fermenting action of yeast juice is due to the presence of living fragments of protoplasm, torn from the cells, which have passed through the filter; he claims that his experiments prove that substances which are toxic to yeast, such as sodium metarsenite, ammonium fluoride, chloroform, or glycerin, if added to yeast juice in sufficient quantity, are equally toxic to the latter, which he thinks would not be true if the fermenting agent were an enzyme.

<sup>1</sup> Ztschr angew. Chem., 1898, 957.

<sup>2</sup> Ber. d. chem. Ges., 31, 2261.

Buchner's report of his recent experiments and his reply to Abeles is in the *Berichte* of January 23, 1899. He says that if the plasma hypothesis is correct, yeast juice subjected to centrifugal motion would separate into an upper layer containing few solid particles of plasma and hence possessing little fermenting power, and a lower layer and sediment containing most of the solid particles of plasma, and hence possessing great fermenting power. His experiments show that after hours of centrifugal motion both layers excite fermentation to the same extent. In another series of experiments Buchner shows that the activity of dried yeast juice is not lessened by keeping it for two months. This could scarcely be true of dried living protoplasm. He then repeats the experiments of Abeles with glycerin and chloroform. Assuming that Abeles had not taken care to bring the yeast particles into thorough contact with these reagents, Buchner provides for this in arranging his apparatus. It is known that glycerin and chloroform dissolve enzymes without injury, but kill living organisms. In parallel experiments the fermenting power of dried yeast juice and of fresh yeast in the presence of an excess of these reagents was tested. Equivalence in the amounts of yeast and of dried yeast juice used was secured by determining the nitrogen in each; their fermenting power was found in all cases to be identical, showing, Buchner claims, that while both the glycerin and the chloroform had killed the yeast, stopping further growth, it had not injured the enzyme present in the yeast cells.

Buchner grants that Abeles is right in saying that mercuric chloride, ammonium fluoride, and sodium metarsenite are as toxic to yeast juice as to the living yeast, but says that these reagents form precipitates, chemical compounds, with the albuminates of the yeast or yeast juice, and probably form chemical compounds with the enzyme; hence they cannot be used to decide between the enzyme and plasma hypotheses in the way in which glycerin and chloroform, which do not form albuminate compounds, may be used. In conclusion, Buchner repeats with great care experiments on heating yeast and yeast juice. Yeast is killed when heated six hours at 85°. Yeast juice was heated eight hours at 85° without impairing its fermenting power.

It would seem that Buchner has established his theory as far as is possible without isolating the zymase; work in this direction is going on under his guidance. In the meantime, A. Wróblewski, of Cracow (without consulting Buchner), has been studying the properties of yeast juice by the method of fractional coagulation. A part of the juice coagulates at 35°, another at 41°, others at 51°, 56°, 59°, 62°, and 68°. The coagu-

lated part does not pass through a Chamberland filter. The filtrate from the coagulate at  $35^{\circ}$  ferments sugar; the filtrate of the coagulate at  $41^{\circ}$  does not; hence, Wróblewski assumes that the enzyme "zymase" is in that portion of the yeast juice which coagulates at  $41^{\circ}$ . He further notes that the albuminate coagulating at  $41^{\circ}$  is the first to be destroyed by the proteolytic enzymes present in the yeast juice.

Whether the enzyme theory is established or not, certainly Buchner's work has shown the assumption of Abeles to lack foundation. Indeed, it would require positive evidence to lead chemists or biologists to accept the idea of living fragments of plasma, of bits torn from cell walls, acting like living organisms.

E. R.

*Report of the Committee on Atomic Weights of the German Chemical Society.*<sup>1</sup>

At a meeting of the executive committee of the German Chemical Society, held on the first of December, 1897, the question was put to them by a commission of analytical chemists, who were meeting at that time in Berlin, which atomic weights should be adopted as a basis for practical analytical calculations.

On motion of Dr. E. Fischer, a commission composed of H. Landolt, W. Ostwald, and K. Seubert was appointed to prepare a report on this subject. The commission, after much preparatory labor, held two meetings at which the selection of a unit for the atomic weights, as well as the values for the individual elements, were thoroughly discussed. Finally they decided unanimously to present the following propositions:

- I. *As a basis for the computation of atomic weights, the atomic weight of oxygen shall be taken to be equal to 16.000, and the atomic weights of the other elements shall be computed on the basis of ratios to oxygen, whether determined directly or indirectly.*
- II. *As atomic weights of the elements, for practical use, the following most probable values, at this time, are proposed:*

Aluminium	Al	27.1	Boron	B	11.
Antimony	Sb	120.	Bromine	Br	79.96
Argon(?)	A	40.	Cadmium	Cd	112.
Arsenic	As	75.	Caesium	Cs	133.
Barium	Ba	137.4	Calcium	Ca	40.
Beryllium	Be	9.1	Carbon	C	12.00
Bismuth	Bi	208.5*	Cerium	Ce	140.

<sup>1</sup> Ber. d. chem. Ges., 31, 2761 (1898).



Chlorine	Cl	35.45	Phosphorus	P	31.0
Chromium	Cr	52.1	Platinum	Pt	194.8
Cobalt	Co	59.	Potassium	K	39.15
Copper	Cu	63.6	Praseodymium(?)	Pr	140.
Erbium(?)	Er	166.	Rhodium	Rh	103.0
Fluorine	F	19.	Rubidium	Rb	85.4
Gallium	Ga	70.	Ruthenium	Ru	101.7
Germanium	Ge	72.	Samarium(?)	Sm	150.
Gold	Au	197.2	Scandium	Sc	44.1
Helium(?)	He	4.	Selenium	Se	79.1
Hydrogen	H	1.01	Silicon	Si	28.4
Indium	In	114.	Silver	Ag	107.93
Iodine	I	126.85	Sodium	Na	23.05
Iridium	Ir	193.0	Strontium	Sr	87.6
Iron	Fe	56.0	Sulphur	S	32.06
Lanthanum	La	138.	Tantalum	Ta	183.
Lead	Pb	206.9	Tellurium	Te	127.
Lithium	Li	7.03	Thallium	Tl	204.1
Magnesium	Mg	24.36	Thorium	Th	232.
Manganese	Mn	55.0	Tin	Sn	118.5*
Mercury	Hg	200.3	Titanium	Ti	48.1
Molybdenum	Mo	96.0	Tungsten	W	184.
Neodymium(?)	Nd	144.	Uranium	U	239.5
Nickel	Ni	58.7*	Vanadium	V	51.2
Niobium	Nb	94.	Ytterbium	Yb	173.
Nitrogen	N	14.04	Yttrium	Y	89.
Osmium	Os	191.	Zinc	Zn	65.4
Oxygen	O	16.00	Zirconium	Zr	90.6
Palladium	Pd	106.			

The following facts are to be noted with regard to the table. The numbers, in general, are given with only so many decimal places that the last one may be regarded as sure; consequently the atomic weights determined by Stas to within 3-6 units in the third decimal place are given with two decimals. The better determined atomic weights besides these, with one decimal, and all less surely determined ones with no decimals. The only exceptions to this rule are nickel, bismuth, and tin, which are marked with an asterisk. In the case of nickel the exception is made to emphasize the undoubted difference between the atomic weights of nickel and cobalt. That of cobalt is almost surely 59.0 and the possible variation from this value is not greater than  $\pm 0.2$ . The atomic weight is surely smaller than that of cobalt, although the value 58.7 is not guaranteed within  $\pm 0.2$ . In order then not to make it appear, through rounding off to 59, that nickel and cobalt have the same atomic weight, the most probable atomic weight,  $\text{Ni} = 58.7$ , is given.



As regards bismuth and tin, the true atomic weights lie probably nearer the values ending in 0.5 than to the whole numbers, although they are not definitely known to within 0.1.

For hydrogen the value 1.008 is to be considered as fixed to within 0.001, but for practical purposes the rounding off to 1.01 is allowable as this change signifies an error of only one-fifth of 1 per cent. The elements whose names are followed by a question mark (?) are uncertain either in regard to their homogeneity or as to whole units in their atomic weights.

Some of the arguments which led to the above conclusions are given by each member of the commission with remarks.

The arguments are in no way new, and mostly historical. As Prof. Ostwald says, "all will agree that there is only one question as to a basis, that between oxygen and hydrogen, and historically no other element has been suggested."

The strongest argument for oxygen is that it forms compounds with almost all other elements, thus rendering direct experimental determination possible, whereas with hydrogen almost all determinations depend upon the ratio between oxygen and hydrogen, or its multiples.

There is a pressing need for a generally adopted atomic weight table, since in various chemical works figures appear which not only differ from each other on account of the unit adopted but even where the same basis is used differences will be found for one and the same element.

In Germany we have at the same time the tables of L. Meyer and K. Seubert on the one hand and that of Ostwald on the other, while in America we have the annually appearing table by F. W. Clarke.<sup>1</sup> In consequence of this state of affairs such uncertainty has arisen as to introduce serious inconvenience in analytical calculation.

It is proposed to issue this table every year with the first number of the *Berichte*, after it has been revised to suit the changes which the work of the year may render necessary.

It is certainly very desirable that an international understanding in this matter should be reached. There should be no serious difficulty about this seeing how few serious differences there are between the figures of Clarke, of Richards,<sup>2</sup> and those of the above table.

C. L. REESE.

<sup>1</sup> J. Am. Chem. Soc., 20, 163 (1898).

<sup>2</sup> This JOURNAL, 20, 543 (1898).

A DIGEST OF METABOLISM EXPERIMENTS IN WHICH THE BALANCE OF INCOME AND OUTGO WAS DETERMINED. BY W. O. ATWATER, Ph.D., AND C. F. LANGWORTHY, Ph.D. Prepared under the supervision of A. C. TRUE, Ph.D., Director of the Office of Experiment Stations. Bulletin No. 45 (Revised Edition). U. S. Department of Agriculture, Office of Experiment Stations.

This work aims to give as complete a digest as possible of all experiments which have been carried on to determine the income and outgo of the animal organism, whether matter or energy. In most cases the balance of nitrogen and carbon was determined, but a number of experiments include phosphorus, sulphur, or other mineral matter. The balance of nitrogen and energy has been determined in a few cases only. A total of 3,661 individual tests or averages is included, 2,299 of which were made with man, the remainder with cattle, horses, sheep, dogs, poultry, doves, etc. The nitrogen balance was determined in 2,234 tests with man, and 1,156 with animals; the balance of carbon and nitrogen in 65 with man and 206 with animals. No attempt was made to include experiments published since 1894. The work purposes to give a brief epitome of the objects and results of individual experiments; tables furnish the framework for this, and supplementary data are given in the accompanying text. The tables are classified first according to the animal, next the balance of nitrogen, as nitrogen and carbon, or nitrogen and energy, and finally subdivided according to the conditions of the experiment. It will be of great assistance to all engaged in investigations on the chemistry and economy of foods. G. S. F.

NEUE GASOMETRISCHE METHODEN UND APPARATE. VON OTTO BLEIER. Spielhagen and Schurich; Wien. 1898.

The author is well known through his many and excellent improvements in gas analytical apparatus and methods, accounts of which have appeared from time to time in the *Berichte* of the German Chemical Society. The present work is mainly concerned with the applications of these improvements to the analysis of gases, though considerable attention is given to the description and discussion of the already existing apparatus and operations which are affected by the author's own inventions and suggestions.

According to the preface, it was the author's first intention to produce an elaborate work which should incorporate his own improvements, and at the same time give a complete summary of the present condition of gasometry. This purpose could not, however, be realized owing to the pressure of other duties. He therefore decided to present, in its incomplete form, the material already collected. This explanation will sufficiently account for the somewhat uneven character of the different parts of the work.

H. N. M.

THE ELEMENTS OF PHYSICAL CHEMISTRY. BY J. LIVINGSTON R. MORGAN, Ph.D., of the Department of Physical Chemistry, Columbia University. First Edition, First Thousand. New York: John Wiley Sons; London: Chapman and Hall. 1899. pp. 299.

The author states that "the object of this book is to present the elements of the entire subject of physical chemistry in one volume, together with the important and but little known applications of it to the other branches of chemistry." The work treats of the solid liquid, and gaseous states of matter, of solutions, rôle of the ions in analytical chemistry, thermochemistry, chemical equilibrium and kinetics, the phase rule, and electrochemistry.

Even considering the very elementary character of the book one is impressed by the entire omission of a number of important chapters. Under liquids no mention is made of Kopp's work on atomic volumes, of the work of Pulfrich, Landolt, Gladstone, Brühl, and others on the refractivity of liquids, of the rotation of the plane of polarized light and the Le Bel-van't Hoff hypothesis, of the work of Perkins and of Rodger and Watson on magnetic rotation, of Thorpe and Rodger on viscosity, of Ramsay and Shields on the surface-tension of liquids as applied to the determination of molecular weights.

The chapter on solutions contains much of value, but in places is not quite accurate. From page 83 one would conclude that artificial semi-permeable membranes were discovered by Pfeffer, when the discovery belongs to Traube. On page 85 we find "equal amounts of solute," instead of equivalent amounts. The boiling-point and freezing-point methods of Beckmann are described, and no mention is made of the large amount of subsequent work, which has greatly improved both of them.

The dilution law of Ostwald is considered (p. 170), while the more recently discovered law of Rudolphi is not mentioned. The latter, although purely empirical, holds as well for the strongly dissociated electrolytes, as the former for the more weakly dissociated, and is probably of equal importance.

The subject of solid solutions seems to merit more than eight lines even in a very elementary book.

The discovery of the relation between the dielectric constants of solvents and their dissociating power is ascribed solely to Nernst, while, in fact, it was pointed out at the same time by J. J. Thomsen. (*Phil. Mag.*, 36, 320.)

The author seems to have drawn for his material rather upon text-books which have been published several years, than upon the current literature; hence some of the omissions.

The reader of the book will be able to obtain an elementary conception of many of the fundamental principles which underlie the science of physical chemistry. HARRY C. JONES.

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### CORRESPONDENCE.

BERLIN, March 30, 1899.

TO THE EDITOR :

With a view to securing agreement in the atomic weights to be used for practical purposes, the German Chemical Society submitted the question for investigation to a Commission and in accordance with its report, has adopted the resolutions appended. The most essential points are these: Oxygen with the value 16.000 shall be taken as the basis of calculation, and for practical purposes the atomic weights shall be expressed with only so many decimal places, that the last can be accepted as correct.

The German Chemical Society is conscious that the task which it set has received only a partial solution, and that the work must be carried forward until agreement in this question prevails in all civilized countries. While it is perhaps not to be expected that agreement will be reached in the recalculation of all the available material and the validity of the atomic weights established to the last decimal place, it seems possible to carry out the more modest task of obtaining agreement in the atomic weights employed in analytical and technical work.

We take the liberty of inviting the chemical Societies and similar Institutions of all countries to assist in the formation of an International Commission, whose task it shall be, to settle this question, either by means of written communications or by personal conference. We would first propose that every Society should elect members, whose names shall be sent to the President of the German Commission, Prof. Dr. Landolt, Berlin NW., Bunsenstrasse 1. As soon as answers to this invitation are received the preparatory steps in the work of the International Commission will be taken. In the meantime the Societies which have accepted the invitation will be advised of the progress of the matter.

The Members of the German Commission on Atomic Weights: H. Landolt, W. Ostwald, K. Seubert.

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### *Corrections.*

Vol. 20, page 327, line 14: *For* "triaxial" *read* "biaxial."

Vol. 20, page 338, line 14 from bottom: *For* "triaxial" *read* "biaxial."

Vol. 21, page 256, line 8: *For* "attainable" *read* "obtainable."

# AMERICAN CHEMICAL JOURNAL

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## THE VALUATION OF SACCHARIN.

BY E. EMMET REID.

About two years ago, at the suggestion of Prof. Remsen, I took up the study of the hydrolysis of acid amides.<sup>1</sup> This was suggested by the work of Remsen and Burton<sup>2</sup> on saccharin, in which it appeared that benzoic sulphinide, when boiled with dilute acids, passes through *o*-sulphaminebenzoic acid into the acid ammonium salt of *o*-sulphobenzoic acid, while *p*-sulphaminebenzoic acid is not affected. In my work it has been customary to estimate the amount of amide decomposed by the amount of ammonia it would yield. From this it was natural to attempt the estimation of benzoic sulphinide in the same way. A number of analyses were made of a specimen of commercial saccharin. In these, 0.750 gram saccharin was boiled with dilute hydrochloric acid and the ammonia determined by distilling with alkali. At first the results were not quite satisfactory. As Hefelmann's<sup>3</sup> work had been brought to my notice it seemed worth while to try 71 per cent sulphuric acid as recommended by him for the hydrolysis.

After making a few analyses with sulphuric acid, I was fortunate in securing the cooperation of Mr. L. B. Mat-

<sup>1</sup> This JOURNAL, 19, 319.

<sup>2</sup> *Ibid.*, 11, 403.

<sup>3</sup> Ph. C., 85, 107; and Ph. C., 1895, No. 16.



tern of this laboratory, an experienced and careful analyst who, for some time past, had been engaged under Professor Remsen's direction, on a comparison of the methods of Remsen and Burton and of Hefelmann. In all of the analyses with sulphuric acid, Mr. Mattern had charge of all except the distillation and titration.

As 1 cc. of the standard acid in hand was equivalent to 26 mg. sulphinide,  $26 \times 25$  or 650 mg. saccharin was taken for each analysis. Then it was only necessary to multiply by 4 the number of cubic centimeters of acid neutralized by the ammonia, in order to obtain the percentage of sulphinide in the sample.

*Method of Analysis with Sulphuric Acid.*

To 0.650 gram saccharin weighed into a test-tube about  $18 \times 160$  mm., was added 10 cc. of 71 per cent sulphuric acid, made by diluting 132 grams pure concentrated acid with 37 cc. of water. The test-tube was loosely closed by a cork through which passed a small glass rod, bent into a loop at the bottom. By means of this the mixture was repeatedly stirred during the three hours' heating. Eight to sixteen of these tubes were suspended in a bath of vigorously boiling water, for three hours. After cooling, the contents of the tube were diluted with water, washed into the distilling flask, 15 grams caustic soda added, and the ammonia distilled off into standard acid.

*Results Stated in Percentages of Benzoic Sulphinide.*

*Sample A—Commercial Saccharin.*

1	54.5	9	55.1	16	55.3	23	55.3
2	54.9	10	55.5	17	55.7	24	55.4
3	54.5	11	55.1	18	55.1	25	55.4
4	55.1	12	55.6	19	55.4	26	55.7
5	55.8	13	55.6	20	55.1	27	54.8
6	55.3	14	55.6	21	55.2	28	55.3
7	55.6	15	55.2	22	55.1	29	55.2
8	55.7						

Nos. 1-4 were experimental. Nos. 20-29 were made entirely by Mr. Mattern with independent standard solutions.



He had previously found 55.2 and 54.7 per cent by Hefelmann's method.

*Sample B—Another Lot of Commercial Saccharin.*

1	94.0	5	94.5	9	95.1
2	94.3	6	94.3	10	95.1
3	94.1	7	95.3	11	95.0
4	94.4	8	94.5	12	94.9

*Sample C—4.600 Grams Pure Sulphinide, Crystallized from Acetone, Mixed with 0.0700 Gram Pure Parasulphaminebenzoic Acid.*

Calculated, 86.8 per cent.

Found.	Found.
1 88.0	4 88.0
2 86.7	5 86.7
3 87.4	6 87.5

*Sample D—4.000 Grams Pure Sulphinide Mixed with 1.500 Grams Pure Parasulphaminebenzoic Acid.*

Calculated 72.7 per cent.

Found.	Found.
1 72.5	5 72.9
2 73.6	6 73.3
3 73.3	7 73.6
4 73.5	8 73.1

*Sample E—A Beautiful Specimen of Commercial Saccharin.*

Found.	Found.
1 98.7	5 98.9
2 99.1	6 99.3
3 98.5	7 98.9
4 98.8	Av. 98.9

*Sample F—Another Specimen of Commercial Saccharin.*

Found.	Found.
1 89.0	4 89.2
2 89.4	5 88.6
3 89.6	

*Sample G—Pure Benzoic Sulphinide from Acetone.*

Found.	Found.
1 99.1	4 99.7
2 99.7	5 98.8
3 98.9	Av. 99.2

The following mixtures were made up from pure sulphinide and pure parasulphaminebenzoic acid :

No.	Sulphinide. Gram.	Para Acid. Gram.	Per cent calc.	Per cent found.
1	0.5291	0.1209	81.4	82.2
2	0.5328	0.1172	82.0	82.0
3	0.4971	0.1529	76.5	79.1
4	0.5197	0.1303	79.9	80.9
5	0.5026	0.1474	77.3	78.9
6	0.5036	0.1464	77.5	78.1
7	0.5316	0.1184	81.8	81.7
8	0.3381	0.3119	52.0	53.5
9	0.3431	0.3069	52.8	53.5
10	0.3518	0.2982	54.1	55.2
11	0.4194	0.2306	64.5	62.4
12	0.4168	0.2332	64.1	64.6
13	0.5208	0.1292	80.2	79.6

*Experiments with Pure Parasulphaminebenzoic Acid.*

The acid used in these, as in other analyses in this work, was kindly furnished me by Mr. J. S. Chamberlain, of this laboratory, who has for some time past been investigating that substance. The sample was considered by him to be absolutely pure.

0.300 gram pure parasulphaminebenzoic acid was weighed into each of eight test-tubes, heated in the usual manner with 71 per cent sulphuric acid, and distilled with caustic soda. The results are given in cubic centimeters of  $\frac{1}{N}$  acid.

1	0.27	6	0.29
2	0.19	7	0.27
3	0.27	8	0.27
4	0.27	Blank	0.05
5	0.29	Average minus blank, 0.21	
		cc. equivalent to 0.51 mg.	
		ammonia, or 5.9 mg. para-	
		sulphamine acid.	

These results seem to show that parasulphaminebenzoic acid is slightly hydrolyzed by 71 per cent sulphuric acid at 100° C. This is supported by the generally high results of the test mixtures above.

Several other samples of pure parasulphaminebenzoic acid with 71 per cent sulphuric acid were overheated by the water-

bath accidentally going dry. In one of these, 86 per cent of the acid was found to be hydrolyzed. These results led me to return to hydrochloric acid and to devise the method described below.

*Method of Analysis.*

0.650 gram saccharin is weighed into a 100 cc. Florence flask and 50 cc. dilute hydrochloric acid added. This acid is prepared by diluting 120 cc. pure concentrated hydrochloric acid to 1 liter. The flask is fitted with a cork through which passes a glass tube 8 mm. wide and 45 cm. long. The flask is placed on a sand-bath and allowed to boil gently for two hours. Eight of these flasks can be heated conveniently on one sand-bath and require only occasional attention. The stopper is removed and the solution allowed to evaporate down to about 10 cc. After diluting, the contents of the flask are washed into the usual distilling flask and 20 cc. added of a solution containing 0.5 gram caustic soda in 1 cc. (or 10 grams of caustic soda). The ammonia is distilled off into standard acid and the excess titrated back with aqueous caustic potash, cochineal being used as indicator. After neutralizing, 0.20 or 0.30 cc. standard acid is added and the neutral point again determined, the two results being averaged. For a distilling flask, a 500 cc. pear-shaped digesting flask serves best. Steam is passed in from a large flask containing water with a little potassium bichromate and sulphuric acid. The steam is a great advantage, as it causes even very concentrated solutions of caustic soda loaded with salts to boil nicely. In nearly a thousand analyses carried on with these flasks with steam only two have broken.

Standard acid about  $\frac{1}{7}$  N is the most convenient. 25 cc. of this is put into the receiver each time. If the saccharin is known to be of low grade less may be used.

The following analyses were made by this method :

*Sample H—Pure Benzoic Sulphinide.*

Prepared in exactly the same way as Sample G. Both prepared by Mr. Mattern.

1	100.8	5	99.3
2	100.4	6	99.4
3	100.6	7	100.2
4	100.5	Av.	100.2

No. 5 went to dryness with the hydrochloric acid.

The excess over 100 per cent is due to ammonia in the reagents and to errors of burettes, etc. When calculated for nitrogen, No. 1 appears thus :

	Calculated.	Found.
N	7.65	7.71

It is important to notice that the average is just 1 per cent higher than was found for Sample G with sulphuric acid.

The same burettes, standard solutions, etc., were used in both cases. It seems fair to conclude that by the above treatment with hydrochloric acid benzoic sulphinide is more completely hydrolyzed, and yields more ammonia than when heated with 71 per cent sulphuric acid at 100° C. for three hours.

The following test mixtures were made up and analyzed. Into each was weighed 500 mg. sulphinide and 150 mg. para acid :

Calculated, 76.9.

Found.	Found.
1 77.6	5 76.4
2 77.4	6 77.6
3 77.5	7 77.4
4 77.2	

Into each was weighed 450 mg. sulphinide and 200 mg. para acid.

Calculated, 69.2.

Found.	Found.
1 69.2	5 68.8
2 69.3	6 68.4
3 69.0	7 69.1
4 69.3	8 69.1

*Sample A—Commercial Saccharin.*

Found.	Found.
1 54.6	6 54.1
2 54.2	7 54.0
3 54.1	8 54.4
4 55.0	9 54.2
5 54.2	Av. 54.3

These results are on the average 1 per cent lower than those obtained with sulphuric acid, which must have converted a little of the large amount of para acid present.

*Sample I—Commercial Saccharin from the Same Can as B, but from Another Part of the Can.*

1	76.7	5	76.2
2	77.2	6	74.9
3	77.3	7	76.2
4	76.9	8	76.4

*Sample J—Commercial Saccharin.*

1	99.0	4	99.2
2	98.6	5	99.7
3	98.8	6	99.0

*Sample K—Commercial Saccharin.*

(Only 1.23 gram in hand.)

1	96.9	2	96.7
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*Sample E—Commercial Saccharin.*

1	99.7	5	99.9
2	99.7	6	99.7
3	99.8	7	99.2
4	99.8	Av.	99.7

Here the average is 0.8 per cent higher than average of analyses of same sample with sulphuric acid. Compare analyses of pure saccharin.

*Experiments with Pure Parasulphaminebenzoic Acid.*

0.300 gram of the pure acid weighed into each of six flasks, heated in the usual manner with hydrochloric acid and distilled with 10 grams caustic soda. The results are given in cubic centimeters of  $\frac{1}{7}$  N acid neutralized.

1	0.02	5	0.04
2	0.02	6	0.05
3	0.02	7	0.04
4	0.02	8	0.05

Average 0.03 cc. Blank with reagents 0.03 cc. Parasulphaminebenzoic acid is not acted upon by hydrochloric acid under these conditions.

Experiments were next undertaken to determine the approximate rate of hydrolysis and to test the completeness of the reaction when carried on according to Remsen and Burton. 0.650 gram of a sample of commercial saccharin was weighed into each of eight flasks, with 50 cc. of dilute acid (1 part of pure concentrated hydrochloric acid to 8 parts water). The six flasks were placed on a sand-bath and began to boil at nearly the same time :

No. 1	boiled about thirty-three minutes,	found	69.3
" 2	" " forty-five	" "	81.6
" 3	" " sixty	" "	84.5
" 4	" " "	" "	87.0
" 5	} boiled about 60 minutes and evapora-	{	93.6
" 6			ted down to 10 cc.

Analyses of the same specimen by the usual method gave about 94 per cent. The hydrolysis was complete in 5 and 6. Remsen and Burton boiled 2 grams saccharin with 200 cc. of this strength hydrochloric acid and evaporated down to 15 cc., which was more thorough treatment than Nos. 5 and 6 received. From these experiments I am unable to account for the fact that Hefelmann found only about 93 per cent, as much ammonia by the method of Remsen and Burton as by his own.

#### *Action of Caustic Soda on Saccharin.*

Boiling caustic soda solution quite readily converts benzoic sulphinide into the sodium salt of *o*-sulphaminebenzoic acid but does not break this acid down. In twelve experiments boiling 650 mg. of Sample A, a very low grade specimen, with 10 grams caustic soda in from 75 to 150 cc. of water, for one and a half to two hours, only a few tenths of a milligram of ammonia was found in each case. This was probably not due to the benzoic sulphinide present. This was shown by boiling 650 mg. of Sample E in the same way by which only 0.05 mg. ammonia was found. This is about the amount found in a blank. To the residue in the distilling flask an excess of hydrochloric acid was added and the whole boiled for several hours and evaporated down. As the solution contained much sodium chloride there was a little spattering, but on adding an excess of caustic soda and



distilling, an amount of ammonia corresponding to 98.5 per cent sulphinide was found. Previous analysis in the usual way gave 99.7 per cent. This is of importance, as it suggests that the sulphinide may be estimated, with fair accuracy, in the presence of salts of ammonia or of other volatile bases or of benzamide, and many of its substitution-products, of amides of fatty acids, or of anything else which is readily broken down by boiling with 10 or 15 per cent caustic soda.

To test this the following experiment was made. Unfortunately, it was not very successful and would have been repeated but for lack of time. The following mixture was made up: 0.1478 gram pure ammonium chloride, 0.5000 gram pure *p*-nitrobenzamide, 0.6500 gram pure benzoic sulphinide, 0.3750 gram pure *p*-sulphaminebenzoic acid, 4 grams magnesium chloride, and 0.5 gram caustic soda were added and the whole distilled.

	Calculated. mg.	Found.
NH <sub>3</sub>	47.1	47.9

5 grams caustic soda added and distilled again. Found 51.1 mg. NH<sub>3</sub> corresponding to 499 mg. out of 500 mg. *p*-nitrobenzamide. The contents of the flask were neutralized with hydrochloric acid and about 8 cc. of concentrated hydrochloric acid added. The solution was boiled for several hours and allowed to evaporate down. An excess of caustic soda was added and the ammonia distilled off. This was found to correspond to 99.1 per cent of the saccharin put in. The flask was removed, an excess of pure sulphuric acid added and heated. Unfortunately, it was heated too high, so that slight charring took place, and not only the parasulphaminebenzoic acid was broken down but some little of the *p*-nitrobenzoic acid was also acted upon. On adding excess of caustic soda and distilling, 36.2 mg. ammonia was obtained instead of 33.7 mg. ammonia, representing the para acid. Had this not been overheated it would have been possible to have estimated the nitrogen in the nitro-group by the Kjeldahl process. Hence there are, at least, five classes of nitrogen compounds, of which the above are representatives, the nitrogen of which can be successively and independently estimated in the same solution. This suggests the inorganic groups.

*Analysis of Pure Parasulphaminebenzoic Acid.*

To hydrolyze this acid completely it is unnecessary to use any of the modifications of the Kjeldahl process. Heating with pure concentrated sulphuric acid alone is sufficient.

0.3000 gram of the pure parasulphaminebenzoic acid was weighed into each of the two test-tubes. To each was added 5 cc. pure concentrated sulphuric acid. The two tubes were placed in a beaker containing sulphuric acid and heated several hours at from  $230^{\circ}$ – $260^{\circ}$  C. The contents of the tubes were distilled with caustic soda in the usual way and gave (1) 25.73 mg. ammonia and (2) 25.57 mg. ammonia. Subtracting 0.12 mg., the amount of ammonia found with nearly the same amount of reagents, these figures give:

1. 8.54 per cent  $\text{NH}_3$ .
2. 8.49 per cent  $\text{NH}_3$ .
- Calc. 8.46 per cent  $\text{NH}_3$ .

It seems likely that the hydrolysis might be complete at a much lower temperature. By heating with concentrated sulphuric acid alone and only to such temperature as might be found sufficient, parasulphaminebenzoic acid might be estimated in the presence of many nitrogenous bodies.

*General Remarks.*

One advantage in the use of hydrochloric acid is that, from first to last, during the heating the whole sample of saccharin is completely in solution, and much more uniform and certain action may be expected. While the use of hydrochloric acid is preferred yet the 71 per cent sulphuric acid, when used as above directed, gives very nearly the same results.

The estimation of sulphinide according to this method is much simpler and quicker than the ordinary Kjeldahl analysis for nitrogen and seems capable of the same proportionate accuracy.

As the percentage of nitrogen is multiplied by 13 to obtain the percentage of sulphinide, the absolute error is multiplied by the same factor. As a variation of 0.2 per cent on 100 per cent, or 1 part in 500 is allowable, it is useless to weigh the sample of saccharin with great accuracy. 0.2 or 0.3 of a

milligram either way makes little difference. I have weighed 8 samples of 0.650 gram  $\pm 0.0003$  gram in sixteen minutes. To hydrolyze 10 grams saccharin according to Hefelmann, filter, wash, dilute to 500 cc., and measure out portions for the estimation of ammonia, is certainly more troublesome. The weight of sample taken, strength of solutions, etc., are not essential to the method but are capable of wide variation. It is hoped that what has been done may lead to the more general and accurate valuation of commercial saccharin as well as to the detection and estimation of saccharin in many substances, both liquid and solid, in which this substance might be used. The method in one form or another seems capable of wide application, but the limits and conditions of its use must yet be determined.

CHEMICAL LABORATORY,  
JOHNS HOPKINS UNIVERSITY,  
June, 1898.

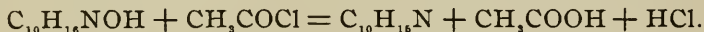
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Contributions from the Chemical Laboratory of the University of Minnesota.

## SOME DERIVATIVES OF CAMPHOROXIME.

BY G. B. FRANKFORTER AND A. D. MAYO.

As stated by Naegli,<sup>1</sup> camphoroxime forms derivatives characteristic of the common acetoximes, differing, however, by their unusual stability and by their tendency to crystallize. Of the derivatives, the hydrochloride,  $C_{10}H_{16}NOH.HCl$ , the sodium salt,  $C_{10}H_{16}NONa$ , and the ethyl ester,  $C_{10}H_{16}NOC_2H_5$ , were prepared. No derivatives, however, were made from the acids, the oxime remaining unchanged even with the strong mineral acids. With the organic acid chlorides, a peculiar reaction was observed, the result of which was the formation of hydrochloric acid, acetic acid, and camphornitril or so-called anhydride, according to the following equation:



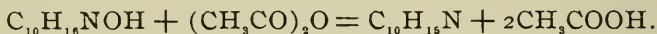
This so-called anhydride is a liquid at the ordinary temperature, with an agreeable odor and a boiling-point of  $216^\circ$  to  $218^\circ$  C. It changes to campholenic acid according to the common nitril reaction.

With acid anhydrides, the same tendency to break off a

<sup>1</sup> Ber. d. chem. Ges., 16, 2981.

molecule of water, was observed by the characteristic odor of the nitril. However, if conditions are favorable, they form esters, all of which show a greater or less tendency to break down into the nitril.

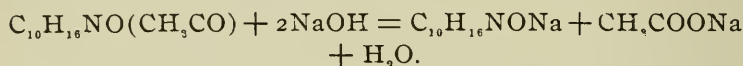
*Acetylcamphoroxime*,  $C_{10}H_{16}NO(CH_3CO)$ .<sup>1</sup>—Acetic anhydride reacts upon camphoroxime readily. If heated with excess, it forms the nitril as indicated by the odor and by the boiling-point :



If, however, the oxime is treated with the anhydride and allowed to stand for some time in a desiccator, the almost pure ether is formed :



The purified substance has an aromatic odor and the boiling-point,  $170^\circ C$ , decomposing and turning black at that temperature. The oil is insoluble in water, but slowly decomposes, forming acetic acid and the oxime. With sodium hydroxide the substance readily saponifies, forming sodium acetate and the sodium salt of the oxime :<sup>2</sup>



By carefully neutralizing the sodium salt with hydrochloric acid camphoroxime is liberated. Analysis of the purified substance gave the following results :

I. 0.1866 gram of the substance gave 0.4688 gram  $CO_2$ , and 0.1554 gram  $H_2O$ .

II. 0.2338 gram of the substance gave 0.5862 gram  $CO_2$ , and 0.2156 gram  $H_2O$ .

	Calculated for $C_{10}H_{16}NO(CH_3CO)$ .	I.	Found. II.
C	68.89	68.52	68.39
H	9.09	9.25	10.24

*Chloralcamphoroxime*,  $(C_{10}H_{16}NO)_2CHCl + 2H_2O$ .—Camphoroxime treated with chloral alone evidently forms several different substances. If, however, the chloral be added to an ether solution of the oxime and allowed to stand until the

<sup>1</sup> Proc. Chem. Soc., 1897, 135.

<sup>2</sup> Part of Thesis presented by A. D. Mayo for M. S. degree, 1896.

ether has evaporated, a waxy substance remains, which, when stirred with an excess of water, readily becomes a solid, crystalline mass. Purified from alcohol, the substance formed a fine, white, crystalline powder, melting at  $82^{\circ}$ . It decomposes at the same temperature, and is likewise readily broken up by alkalies. It contains water of crystallization, all of which cannot be removed without decomposition. It decomposes slowly on standing over sulphuric acid. It is inodorous but has the taste of camphor. It is soluble in ether and alcohol, but insoluble in water. An analysis gave the following :

0.2427 gram of the substance gave 0.4748 gram  $\text{CO}_2$ , and 0.1616 gram  $\text{H}_2\text{O}$ .

	Calculated for $(\text{C}_{10}\text{H}_{16}\text{NO})_2\text{CHCCl}_3 + 2\text{H}_2\text{O}$ .	Found.
C	52.85	53.33
H	7.40	7.39

*Succinylcamphoroxime*,  $\text{C}_{10}\text{H}_{16}\text{NOOCCH}_2\text{CH}_2\text{COOH}$ .—Camphoroxime, in ether solution, was treated with succinic anhydride on a water-bath with reflux condenser and with constant stirring, for twenty-four hours. On removing the ether a heavy colorless and almost inodorous oil remained. Excess of the anhydride was removed by redissolving in a small quantity of ether, filtering, and treating with an excess of warm water. Boiling with water or treating with alkalies breaks it up into the oxime and succinic acid. The oil thus purified appeared quite stable, boiling at  $246^{\circ}$ , with decomposition. On standing over sulphuric acid for several weeks the substance began to decompose, changing from a colorless oil to a substance looking like glue. Two analyses gave the following numbers :

I. 0.1915 gram of the substance gave 0.4460 gram  $\text{CO}_2$ , and 0.1540 gram  $\text{H}_2\text{O}$ .

II. 0.1624 gram of the substance gave 0.3761 gram  $\text{CO}_2$ , and 0.1186 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{10}\text{H}_{16}\text{NOOCCH}_2\text{CH}_2\text{COOH}$ .	I.	Found. II.
C	62.92	63.51	63.15
H	7.86	8.91	8.17

## CAMPHOROXIME DERIVATIVES.

BY G. B. FRANKFORTER AND P. M. GLASOE.

As already stated, camphoroxime, treated with certain acid anhydrides, forms esters of the respective acids. In some cases the reaction took place with greater or less difficulty, while in others the ester was readily formed together with a small quantity of the camphor nitril.

*Phthalylcamphoroxime*,  $C_{10}H_{16}NOOCC_6H_4COOH$ .—Camphoroxime remains unchanged if heated for several hours with phthalic anhydride in an ether solution. If, however, benzene or toluene is substituted for ether and the substances heated for several hours in one of these solvents with an excess of the anhydride, a reaction takes place, forming the ester, a part of which crystallizes out if a limited amount of the solvent is used. The ester thus formed contained some free phthalic anhydride, which was partly removed by redissolving in benzene and the last trace removed by heating with water. The substance thus purified melted at  $135^{\circ}.5$ , decomposing at that temperature and liberating phthalic acid and the nitril. It is soluble in ether, alcohol, and chloroform, and readily so in benzene. It is insoluble in carbon disulphide. It crystallizes from dilute alcohol in fine, white needles. Sodium hydroxide readily breaks it up into the oxime and phthalic acid. Various attempts to isolate the sodium salt failed. Heated in boiling alcohol, it slowly changes to the camphor nitril and phthalic acid. At the same time a small quantity of a colorless, inodorous oil was obtained which, although not analyzed, was, in all probability, an ethyl ester of the phthalylloxime. An analysis of the purified crystals gave the following results :

0.1322 gram of the dried substance gave 0.3319 gram  $CO_2$ , and 0.0851 gram  $H_2O$ .

	Calculated for $C_{10}H_{16}NOOCC_6H_4COOH$ .	Found.
C	68.57	68.47
H	6.66	7.14



*The Action of Formaldehyde on Camphoroxime.*

*Camphorformaldoxime*,  $C_{10}H_{16}NOCH_2OH + H_2O$ .—Camphoroxime remains apparently unchanged when treated with formaldehyde in the cold, but when heated on a water-bath with a reflux condenser for several hours, fresh aldehyde being added from time to time, the oxime changes to an oil with the odor both of aldehyde and the oxime. On standing for some time in the air it changes into a solid mass, still holding, however, some free aldehyde. An attempt to analyze both the oil and the solid substance failed, as results were obtained varying all the way from 1 to 3 molecules of the aldehyde to one of the oxime.

The oil was then placed in a large quantity of water and allowed to remain for several days, when beautiful, large, white crystals appeared. These crystals were filtered off and examined. The substance no longer contained free aldehyde. It melted at  $62^\circ$  to  $63^\circ$ . It proved to be comparatively stable, being readily recrystallized out of water in large flakes. If boiled, however, for some time, in water, it breaks down into the oxime and aldehyde. Strong acids also break it down into the same substances. It contains 1 molecule of water of crystallization, which can be removed by heating for some time at a temperature of  $50^\circ$ , or by drying over sulphuric acid for several hours.

0.3542 gram of the substance, dried to constant weight over sulphuric acid, lost 0.1105 gram.

	Calculated for $C_{10}H_{16}NOCH_2OH + H_2O$ .	Found.
$H_2O$	8.37	8.2

Analysis of the substance dried over sulphuric acid gave the following numbers:

I. 0.1811 gram of the substance gave 0.4402 gram  $CO_2$ , and 0.1667 gram  $H_2O$ .

II. 0.2345 gram of the substance gave 0.5799 gram  $CO_2$ , and 0.2042 gram  $H_2O$ .

III. 0.1913 gram of the substance gave 13.2 cc. of N at 739 mm. pressure and  $23^\circ$ .

	Calculated for $C_{10}H_{16}NOCH_2OH$ .	I.	Found. II.	III.
C	67.00	67.04	67.44	....
H	9.64	10.10	9.68	....
N	7.10	....	....	7.6

Great difficulty was experienced in obtaining the large, flaky crystals. Sometimes they formed readily, while at other times it was next to impossible to obtain them. It was found necessary to heat the oxime a definite length of time with slight excess of the aldehyde. The oxime thus heated for eight hours on a water-bath completely changed to the oil. Heated longer than that time, the tendency to form the nitril was apparent; at the same time camphoroxime was formed.

*Camphorparaformaldoxime*,  $C_{10}H_{16}N(C_3H_5O_3)$ .—As stated above, camphoroxime, treated with formaldehyde, dissolves, and forms an oil which gave variable results on analysis, but from which the formyl compound was obtained. If, however, the oxime is heated with an excess of the aldehyde and allowed to stand in a warm place and in the direct rays of the sun, a thick oily substance is formed which floats on the aldehyde. This oil was separated by extracting with ether, and then examined. The oil, purified by extraction with ether, had the odor of camphor, and, at the same time, that of formaldehyde. If kept over sulphuric acid for several days, it breaks down into camphoroxime and the aldehyde. The decomposition does not take place if the substance is kept cold. Dropped into water containing a little formaldehyde, it changes readily into the formyl compound, as indicated by the form of crystal, and by the melting-point. At the same time another substance was formed which remained in the aldehyde solution and which was identified as paraformaldehyde. Analysis of the oil which had been purified from ether gave the following results :

I. 0.2060 gram of the oil gave 0.4918 gram  $CO_2$ , and 0.1688 gram  $H_2O$ .

II. 0.2265 gram of the oil gave 0.5398 gram of  $CO_2$ , and 0.1896 gram  $H_2O$ .

	Calculated for $C_{10}H_{16}N(C_3H_5O_3)$ .	I.	Found. II.
C	65.27	65.10	64.99
H	8.78	9.10	9.3

*The Action of Sulphothionyl Chloride on Camphoroxime.*

Sulphothionyl chloride acts violently on camphoroxime, undoubtedly forming with it several different compounds. If, however, the chloride be diluted with ether, the reaction is less violent, and a monochlor derivative of camphoroxime is formed. This substance, when first obtained, showed the presence of sulphur, but an analysis<sup>1</sup> revealed only a mere trace which was afterwards removed by recrystallization. Several attempts to obtain the sulpho compound failed, although indications of such a substance were observed on treating the oxime with the liquid chloride alone.

*Monochlorcamphoroxime*,  $C_{10}H_{16}ClNOH$ . — Camphoroxime was dissolved in ether and sulphothionyl chloride cautiously added. A reaction began immediately and a fine, amorphous powder was precipitated. If the chloride is diluted with ether and added drop by drop, the substance appears as fine needle-shaped crystals. So perfectly insoluble was the substance in ether that the reaction was quantitative. Two grams of the oxime dissolved in 50 cc. of ether and an excess of the chloride added, gave 2.3 grams of the chloride. The substance thus obtained was a fine, white, crystalline powder, readily soluble in methyl and ethyl alcohols and water. The substance was purified by dissolving in a small quantity of alcohol and precipitated by adding ether. Thus precipitated and dried, the substance melted at  $290^{\circ}C$ . It contained no water of crystallization. Analyses of the dried substance gave the following results :

I. 0.1737 gram of the dried substance gave 0.3860 gram  $CO_2$ , and 0.1494 gram  $H_2O$ .

II. 0.1148 gram of the dried substance gave 0.2560 gram  $CO_2$ , and 0.0872 gram  $H_2O$ .

III. 0.1188 gram of the dried substance gave 0.08756 gram  $AgCl$ .

IV. 0.1133 gram of the dried substance gave 0.07985 gram  $AgCl$ .

<sup>1</sup> 0.4100 gram of the chloride gave 0.0076 gram of  $BaSO_4$ .

	Calculated for $C_{10}H_{15}ClNOH$ .	I.	II.	Found. III.	IV.
C	59.55	60.6	60.81	....	....
H	7.94	8.55	8.43	....	....
Cl	17.63	....	....	17.48	18.29

Up to the present nothing has been determined concerning the position of the chlorine. Several isomeric forms are possible. The chlorine has been removed, both by silver oxide and by sodium hydroxide, and the products are now under examination.

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## THE LABORATORY PRODUCTION OF ASPHALTS FROM ANIMAL AND VEGETABLE MA- TERIALS.<sup>1</sup>

BY WM. C. DAY.

By carrying out operations of distillation at the ordinary atmospheric pressure upon animal and vegetable matter, both separately and mixed, I have succeeded during the past year in producing three different materials, all of which present in different degrees the properties characteristic of asphalts. Two of these materials quite closely resemble asphalts occurring in nature; *viz.*, gilsonite and elaterite as found in Utah.

Postponing for the present a consideration of the reasons which led to these experiments, I will first give a description of the work done and a statement of the results obtained since the publication, last summer, of a preliminary paper<sup>2</sup> on the same subject.

The first experiment was to distil from an iron retort a mixture of fresh fish (herring from the Delaware) and fat pine wood partly in the form of sawdust and partly in sticks. The retort was connected with a short glass tube by means of a joint of plaster of Paris and asbestos; this tube was connected at the other end by a similar joint with a small iron gas pipe four feet long, placed upon a combustion furnace by which it could be maintained at a red heat. The retort was heated by gas furnaces and the distillation was carried to complete carbonization of the organic matter. An ordinary Liebig's

<sup>1</sup> Published by permission of the U. S. Geological Survey. Read at the stated meeting of the Chemical Section of the Franklin Institute, Feb. 21, 1899.

<sup>2</sup> Proc. Amer. Phil. Soc., 37, 171.

condenser served to condense the mixed oil and water as it issued from the red hot gas pipe. The distillation-product consisted of water of a yellowish-red color, and a dark, nearly black, mobile oil which for the greater part floated upon the water, although toward the close of the distillation a little oil would usually sink through the water.

Twelve operations of distillation consumed 9,882 grams of wood and 8,170 grams of fish and yielded 3,010 cc. oil of sp. gr. 0.9837 and 8,240 cc. water. The average distillation shows, therefore, the figures 823.5 grams wood, 680.8 grams fish, 250.8 cc. oil, and 686.7 cc. water. These average figures were approximated in each single distillation.

The oil was separated from the water and then dried by standing over chloride of calcium. A combustion of this oil, using copper oxide and lead chromate, gave the following results :

0.3104 gram oil gave 0.9593 gram  $\text{CO}_2$ , ; and 0.2794 gram  $\text{H}_2\text{O}$ , or carbon 84.28 per cent, and hydrogen 10 per cent.

The dried oil was then subjected to distillation by itself in a hard glass retort provided with a thermometer. A few drops of oil accompanied by a little moisture came over at  $80^\circ \text{C}$ . ; the temperature rose rapidly to  $120^\circ$ , at which point distillation proceeded rapidly, giving a distillate lemon-yellow in color and slightly turbid from moisture. The receiver was changed at  $180^\circ$ , when the distillate appeared darker in color but free from moisture. The receiver was changed at  $245^\circ$ ,  $315^\circ$ , and  $340^\circ$ , at which last point the thermometer was removed ; after this the distillation was conducted to about  $425^\circ$ , as nearly as could be judged by the rate at which the temperature had been rising. At  $315^\circ$  a greenish fluorescence appeared. When the boiling was stopped the contents of the retort consisted of a mobile, homogeneous, black liquid containing no solid particles of any kind. When the retort cooled, this oil solidified to a black, shining mass, showing conchoidal fracture, brittle, and pulverizing to a brownish-colored powder slightly darker than the powder of Utah gilsonite, which it closely resembled ; in fact it was only by the rounded surface of the artificial product that the two could be distinguished by inspection. A number of distilla-

tions were made with essentially the same experience as just described, except that the material obtained the first time was slightly sticky to the touch and entirely soluble in carbon bisulphide, while the samples obtained subsequently were not at all sticky, and were not entirely soluble in the bisulphide.

Subjected to combustion, the sample resulting from the first distillation gave the following result :

0.2211 gram substance gave 0.7100 gram  $\text{CO}_2$  ; and 0.1540 gram  $\text{H}_2\text{O}$  ; or carbon 87.57 per cent, hydrogen 7.74 per cent.

Two combustions of the artificial gilsonite, finally made in quantity, gave the following results :

I. 0.2529 gram substance gave 0.8031 gram  $\text{CO}_2$ , and 0.1599 gram  $\text{H}_2\text{O}$ .

II. 0.3015 gram substance gave 0.9564 gram  $\text{CO}_2$ , and 0.1938 gram  $\text{H}_2\text{O}$ .

	I.	II.
Carbon	86.61	86.51
Hydrogen	7.02	7.10

Two nitrogen determinations by Kjeldahl's method, using in the first case 1.1990 grams substance, and in the second 0.9824, gave nitrogen 1.95 and 1.86 per cent, respectively.

Two determinations of sulphur by Peckham's method<sup>1</sup> resulted as follows :

I. 2.0218 grams substance gave 0.0136 gram  $\text{BaSO}_4$ .

II. 1.9988 grams substance gave 0.0114 gram  $\text{BaSO}_4$ .

	I.	II.
S	0.092	0.078

According to the figures obtained the composition of the artificial gilsonite appears to be as below. For the sake of comparison, the figures for natural Utah gilsonite are also given here as well as elsewhere.

	Artificial.	Natural.
Carbon	86.56	85.83
Hydrogen	7.06	10.59
Nitrogen	1.91	2.59
Sulphur	0.08	0.26
Oxygen (by diff)	4.39	0.63
	Ash	0.10
	100.00	100.00

<sup>1</sup> Jour. Soc. Chem. Ind., 16, No. 12, 1897.



While the differences in composition between these two materials are not great, still they can by no means be regarded as insignificant, particularly as regards the hydrogen and oxygen. It is true, however, that much greater differences between two natural asphalts taken from sources in the same neighborhood have been found.

Determinations of solubility in the following solvents were made: Carbon bisulphide, turpentine, ether, gasoline, and absolute alcohol. The method employed was to treat a weighed portion of the substance with the solvent until no further action took place, and then weigh the undissolved residue on a tared filter.

*Carbon Bisulphide.*

I.

	Weight.
Substance taken	0.5505
Undissolved residue	0.1060
	<hr/>
Dissolved substance	0.4445
Per cent soluble in $CS_2$ = 80.74.	

II.

	Weight.
Substance taken	0.6970
Undissolved residue	0.1293
	<hr/>
Dissolved substance	0.5677
Per cent soluble in $CS_2$ = 81.44.	

*Turpentine.*

	Weight.
Substance taken	0.9041
Undissolved residue	0.4568
	<hr/>
Dissolved substance	0.4473
Per cent soluble in turpentine = 49.47.	

*Ether.*

	Weight.
Substance taken	0.5776
Undissolved residue	0.1904
	<hr/>
Substance dissolved,	0.3872
Per cent soluble in ether = 67.03.	

*Gasoline.*

	Weight.
Substance taken	0.5339
Undissolved residue	0.2845
	<hr/>
Substance dissolved	0.2494
Per cent soluble in gasoline =	46.71.

*Absolute Alcohol.*

	Weight.
Substance taken	0.5547
Undissolved residue	0.2862
	<hr/>
Substance dissolved	0.2685
Per cent soluble in alcohol =	48.40.

All the solutions obtained were characterized by a more or less marked greenish fluorescence, which is also true of the natural gilsonite.

Solvent.	Action of solvents.	
	Utah gilsonite.	Artificial gilsonite.
Carbon bisulphide	99.50	{ First product 100.00
		{ Second " 81.44
Turpentine	97.34	49.47
Ether	73.08	67.03
Gasoline	63.08	46.71
Alcohol	34.81	48.40

While the above table shows in some cases quite notable differences in solubility, every one of the solvents exercises in each case a pronounced effect, all figures being above 30 per cent and generally nearly 50 per cent or more.

The action of concentrated nitric acid upon the natural and the artificial material is peculiar, and of exactly the same character. This action consists in completely dissolving the material with copious evolution of brown fumes and the production of a dark-red solution, which, when diluted with water, yields a flocculent precipitate much resembling freshly precipitated ferric hydroxide.

In the course of an investigation of Utah gilsonite<sup>1</sup> carried out some years since, I separated from the oils distilled from the mineral certain basic compounds suggestive in odor of the

<sup>1</sup> Jour. Franklin Institute, 140, 221.

pyridine or quinoline series. These bodies were obtained by the extractive action of dilute sulphuric acid upon the oils. From such solution they are thrown down by alkalies as flocculent precipitates.

The same kind of substances were obtained from the oil which by distillation yielded the artificial gilsonite. The method of treatment adopted to extract these basic substances was to shake the oil with dilute sulphuric acid, and then pass steam into the mixture contained in a large flask until oil no longer distilled off with steam. On neutralizing the residual acid with caustic soda solution a precipitate, looking and smelling like that from gilsonite oil, was obtained. The precipitate was alternately redissolved in sulphuric acid and reprecipitated by alkali a number of times and then, after washing with water, was left on a filter to dry. On drying, however, the material largely disappeared, thus showing its volatility, which the solid appearance, when freshly precipitated, had failed to suggest. It is evident, however, that the presence of these basic compounds affords another element of similarity between the natural and the artificial product, and also between these bodies and California petroleum.

#### *Distillation of Fish Alone.*

The interesting character of the product obtained by distilling a mixture of fish and wood, and the similarity between this and Utah gilsonite suggested the advisability of carrying out the same kind of experiments with fish alone, and also with wood alone. Accordingly, a number of charges of the same kind of fish was distilled, using the same apparatus as was employed for the mixture of wood and fish.

In all 4,585 grams of fish were distilled, yielding 700 cc. of oil and 2,830 cc. water. The distillate consisted of a yellow emulsion difficult to break up; the distillate from the fish and wood mixed gave no emulsion at all, but presented a well-defined line of separation between the oil and water. The emulsion was separated into oil and water by heating upon the water-bath, the oil being eventually brought to the surface of the water. Much ammonia was produced during the distillation.

An attempt was made to dry the oil by allowing it to stand over chloride of calcium for a number of days, but it could not be perfectly dried in this way. Success in drying was finally attained only by aspirating a current of dry air through the oil while it was heated upon the water-bath.

On attempting to distil the fish oil from a retort as was done with the oil from the mixture of fish and wood, such vigorous and explosive "bumping" followed as to carry the contents of the retort over mechanically so that it was found impossible to distil it in this way. The appearance of moisture during this attempt to distil an oil which had been thoroughly dried made it evident that the water was formed during the distillation. The oil was transferred from the retort to an iron crucible and heated cautiously until the stage of water formation was passed, and then heated more strongly. After heating for a time, the contents of the crucible were allowed to cool, when a very sticky, thick, semiliquid mass remained. It looked and smelled more like a maltha from Montana that I had examined a few years since, than anything else I could compare it to. The material was again heated in the crucible, it being allowed to boil freely; on cooling again a solid was obtained, black in color and elastic, so that if bent nearly double it would fly back to its original shape like a thick piece of India rubber. It could be easily cut but not pulverized, although if struck a blow with a hammer it would break with conchoidal fracture.

Determinations of carbon, hydrogen and nitrogen were made with the following results:

I. 0.2366 gram substance gave 0.6638 gram  $\text{CO}_2$ , and 0.1933 gram  $\text{H}_2\text{O}$ .

II. 0.2333 gram substance gave 0.6618 gram  $\text{CO}_2$ , and 0.1916 gram  $\text{H}_2\text{O}$ .

III. 0.5233 gram substance gave by Kjeldahl's method ammonia corresponding to 4.19 per cent of nitrogen.

IV. 0.8896 gram substance gave ammonia corresponding to 4.27 per cent nitrogen.

V. 2.0402 grams substance gave 0.0287 gram  $\text{BaSO}_4$ .

VI. 1.9954 grams substance gave 0.0276 gram  $\text{BaSO}_4$ .

	I.	II.	III.	IV.	V.	VI.
Carbon	76.51	77.36	....	....	....	....
Hydrogen	9.08	9.12	....	....	....	....
Nitrogen	....	....	4.19	4.27	....	....
Sulphur	....	....	....	....	0.19	0.19

This material, if cooled down, became harder and less susceptible of bending; the same kind of change seemed to result also as the material became older, as after some months it became harder and more brittle.

The following analytical results were obtained upon a sample of elaterite from Utah. This material, in lump form, was hard and not at all capable of being bent; it was, however, quite flexible when sawed into thin slabs. The percentages of carbon and hydrogen found are not far from those of the asphalt from fish alone.

I. 0.2993 gram substance gave 0.8024 gram  $\text{CO}_2$ , and 0.2550 gram  $\text{H}_2\text{O}$ .

II. 0.1995 gram substance gave 0.5404 gram  $\text{CO}_2$ , and 0.1698 gram  $\text{H}_2\text{O}$ .

	I.	II.
Carbon	73.11	73.88
Hydrogen	9.46	9.45

Further investigation of this material is now being carried out. According to Dana's Mineralogy, p. 734, elaterite, analyzed by Johnston, contains 84 to 86 per cent carbon, and 12.3 to 13.2 per cent hydrogen. I am unable to give the authority for calling the Utah material elaterite, but in composition it evidently resembles much more nearly the material obtained from fish than it does the elaterite described by Dana. The much lower percentage of carbon than is contained in gilsonite is noteworthy.

Treatment of oil obtained from fish alone with dilute sulphuric acid gave a solution of basic nitrogen compounds which could be precipitated by alkalis just as in the case of oil from natural or artificial gilsonite. The odor of these basic substances was of the same character, whatever the source.

The following determinations of the solubility of the asphalt from fish alone were made:

*Carbon Bisulphide.*

	Weight.
Substance used	0.2999
Substance undissolved	0.0954
	<hr/>
Substance dissolved	0.2045
Per cent soluble in $\text{CS}_2$ = 68.19.	

*Turpentine.*

	Weight.
Substance used	0.3163
Substance undissolved	0.1665
	<hr/>
Substance dissolved	0.1498
Per cent soluble in turpentine = 47.36.	

*Ether.*

	Weight.
Substance used	0.2662
Substance undissolved	0.1087
	<hr/>
Substance dissolved	0.1575
Per cent soluble in ether = 59.17.	

*Gasoline.*

	Weight.
Substance used	0.3733
Substance undissolved	0.2419
	<hr/>
Substance dissolved	0.1314
Per cent soluble in gasoline = 35.19.	

*Absolute Alcohol.*

	Weight.
Substance used	0.4239
Substance undissolved	0.2074
	<hr/>
Substance dissolved	0.2165
Per cent soluble in alcohol = 51.07.	

*Distillation of Wood Alone.*

The same kind of rich and heavy pine as was used in mixture with fish was subjected to distillation by itself. In all 4,588 grams were used, yielding 1,150 cc. of oil and 890 cc. water.



It is interesting to note here the much larger proportion of oil obtained than resulted from the distillation of fish alone. The distillation was accompanied by the production of a thick, white smoke which could not be condensed. The distillate was strongly acid. The oil, after drying, showed a specific gravity of 0.992. It was subjected to distillation by itself, the same fractions being collected, as in the case of the distillation of oil from wood and fish. The first fraction,  $90^{\circ}$ – $145^{\circ}$ , was light-yellow in color and slightly turbid from moisture; the second,  $145^{\circ}$ – $180^{\circ}$ , was darker yellow; the third,  $180^{\circ}$ – $245^{\circ}$ , was greenish-black; the last one showed green fluorescence. After distilling off somewhat more than half the oil the black but perfectly mobile liquid was allowed to cool, when it solidified to a black, shining mass, very brittle, and showing conchoidal fracture. While the general color was black, inspection of a thin edge along a line of fracture showed a purple color such as could not be seen with the material from wood and fish. The specific gravity was found to be 1.0825. When pulverized the powder, in the course of several days, would cement together and re-form a hard, rigid mass.

Determinations of carbon, hydrogen, and nitrogen gave the following results :

I. 0.2078 gram substance gave 0.6568 gram  $\text{CO}_2$ , and 0.1549 gram  $\text{H}_2\text{O}$ .

II. 0.9362 gram substance gave ammonia corresponding to 0.26 per cent nitrogen.

III. 0.8884 gram substance gave ammonia corresponding to 0.33 per cent nitrogen.

Determinations of sulphur gave only traces.

	I.	II.	III.
Carbon	86.20	....	....
Hydrogen	8.28	....	....
Nitrogen	....	0.26	0.33

The following determinations of solubility were made :

*Carbon Bisulphide.*

## I.

	Weight.
Substance used	0.3604
Substance undissolved	0.0050
	<hr/>
Substance dissolved	0.3554
Per cent soluble in CS <sub>2</sub> = 98.61.	

## II.

Substance used	0.3868
Substance undissolved	0.0003
	<hr/>
Substance dissolved	0.3865
Per cent soluble in CS <sub>2</sub> = 99.92.	

*Turpentine.*

## I.

	Weight.
Substance used	0.4498
Substance undissolved	0.0155
	<hr/>
Substance dissolved	0.4343
Per cent soluble in turpentine = 96.55.	

## II.

Substance used	0.4218
Substance undissolved	0.0167
	<hr/>
Substance dissolved	0.4051
Per cent soluble in turpentine = 96.04.	

*Ether.*

## I.

	Weight.
Substance used	0.3589
Substance undissolved	0.0153
	<hr/>
Substance dissolved	0.3436
Per cent soluble in ether = 95.45.	

## II.

Substance used	0.4084
Substance undissolved	0.0130
	<hr/>
Substance dissolved	0.3954
Per cent soluble in ether = 96.81.	

*Gasoline.*

## I.

	Weight.
Substance used	0.5342
Substance undissolved	0.0441
	<hr/>
Substance dissolved	0.4901
Per cent soluble in gasoline	91.74.

## II.

Substance used	0.3582
Substance undissolved	0.0412
	<hr/>
Substance dissolved	0.3170
Per cent soluble in gasoline	= 88.49.

*Alcohol.*

	Weight.
Substance used	0.5548
Substance undissolved	0.2130
	<hr/>
Substance dissolved	0.3418
Per cent soluble in alcohol	= 61.60.

High solubility is characteristic of this material in all cases.

A quantity of the oil from wood alone was treated with dilute sulphuric acid for the purpose of testing for basic oils. No trace of these oils could be precipitated, however, by neutralizing the acid with sodium hydroxide.

In connection with the present investigation a complete analysis of Utah gilsonite has been made with results that are somewhat lower in carbon and in sulphur than those obtained and published a few years since.<sup>1</sup> Instead of using finely powdered lead chromate, together with copper oxide, as in the first analysis, a large quantity of coarse granules of lead chromate were employed with results that showed better agreement.

In this connection it should be remarked that the use of copper oxide in combustions of hydrocarbons has not infrequently given trouble in the form of irregularities in the figures for carbon. Professor Peckham, in a recent conversation,

<sup>1</sup> Jour. Franklin Inst., 140, 221.

called my attention to a remark made to him by Warren to the effect that copper forms carbides which are oxidized with difficulty, and hence, according as these are formed or oxidized in succeeding combustions, the figures for carbon will vary. This point is now being investigated. Certain it is, however, that asphalts are troublesome substances in elementary analysis. This statement is thoroughly borne out by a study of the literature of these bodies.

The following are the results of analysis of Utah gilsonite.

I. 0.2738 gram substance gave 0.2603 gram  $H_2O$ , and 0.8631 gram  $CO_2$ .

II. 0.2017 gram substance gave 0.1930 gram  $H_2O$ , and 0.6336 gram  $CO_2$ .

III. 1.0347 grams substance gave ammonia, by Kjeldahl's method, corresponding to 2.65 per cent nitrogen.

IV. 0.9363 gram substance gave ammonia corresponding to 2.53 per cent nitrogen.

V. 2.1651 grams substance gave 0.0390 gram  $BaSO_4$ .

VI. 2.0017 grams substance gave 0.0388 gram  $BaSO_4$ .

	I.	II.	III.	IV.	V.	VI.
Carbon	85.98	85.67	....	....	....	....
Hydrogen	10.56	10.62	....	....	....	....
Nitrogen	....	....	2.65	2.53	....	....
Sulphur	....	....	....	....	0.25	0.27

Taking the averages of these results, the percentage composition appears to be :

Carbon	85.83
Hydrogen	10.59
Nitrogen	2.59
Sulphur	0.26
Oxygen (by diff.)	0.63
Ash <sup>1</sup>	0.10
	<hr/>
	100.00

<sup>1</sup> Quoted from paper on gilsonite : Jour. Frank. Inst., 140, 221.

Table Giving Analytical Results.

Name of substance.	Carbon.	Hydro- gen.	Nitro- gen.	Sul- phur.	Oxy- gen.	Ash.
Oil from fish and wood	84.28	10.00	not determined			none
Artificial gilsonite fr. first preparation	87.57	7.74	"	"		"
Artificial gilsonite made finally	86.56	7.06	1.91	0.08	4.39	"
Utah gilsonite	85.83	10.59	2.59	0.26	0.63	0.10
Asphalt fr. fish alone	76.93	9.10	4.18	0.19	9.60	none
Utah elaterite	73.11	9.45	1.90	3.17	12.37	trace
Asphalt fr. wood alone	86.20	8.28	0.29	trace	5.23	none
Utah nigrite	83.33	8.69		0.42		0.12
	Fixed carbon.		Volatile matter.		Ash.	
Utah nigrite	36.33		63.55		0.12	

The specific gravities of various substances determined in the course of the present investigation are given in the following table :

*Specific Gravities.*

Oil obtained from primary distillation of fish and wood, temperature 26° C.	0.9837
First fraction of above oil 80°-145° C. when distilled by itself, temperature 25.8° C.	0.842
Last fraction in same distillation 340° C., temperature 25.9° C.	1.002
Utah gilsonite, temperature 26° C.	1.0354
Artificial gilsonite, temperature 26° C.	1.1713
Asphalt obtained from wood alone, tem- perature 26° C.	1.0825
Asphalt obtained from fish alone, tem- perature 26° C.	1.0590
Oil from wood and fish volatile with steam, temperature 26° C.	0.8940
Oil obtained in primary distillation of wood, temperature 26.4° C.	0.9920

TABLE OF SOLUBILITIES IN VARIOUS SOLVENTS.

Name of substance.	Carbon bisulphide all. <sup>1</sup>	Turpen- tine.	Ether.	Gasoline.	Absolute alcohol.
Artificial gilsonite	81.09	49.47	67.03	46.71	48.40
Utah gilsonite	99.50	97.34	73.08	63.08	34.81
Asphalt fr. fish alone	68.19	47.36	59.17	35.19	51.07
Asphalt fr. wood alone	99.26	96.29	96.13	90.12	61.60

<sup>1</sup> This determination involved no weighings, as when the solution was filtered, nothing insoluble remained on the filter.

The foregoing experiments suggested themselves as the result of a number of years of experimental work upon asphalts from a number of natural sources in the western part of the United States, and a study of the literature of natural hydrocarbons, solid, liquid, and gaseous, and the synthetical experiments which have been carried out by Warren, Engler, and Sadtler. From the chemical-geological standpoint the writings of Peckham have been very suggestive, advocating as they have done, the idea that bitumens are distillates together with water of organic matter which has accumulated in strata of all ages in the earth.

Utah gilsonite is the natural material to which the writer has given most experimental study. This mineral contains very little oxygen and sulphur, almost no ash, but a notable quantity of nitrogen which shows itself in distillation-products in the form of basic substances similar in a general way to the pyridine and quinoline series, and of the same character as the basic substances obtained by Peckham and Salathé from California petroleum, and freely commented upon by Peckham in a number of papers by him.

These nitrogen compounds suggest that the bodies containing them are of animal origin. It seemed, however, to the writer that a material of exclusively animal origin would be likely to contain a larger proportion of oxygen than is contained in such material as natural gilsonite, and that in laboratory experiments to reproduce asphalts low in oxygen, vegetable material should be present at the same time, and that opportunity should be afforded for the oxygen containing distillates from oils and animal substances to react at a fairly high temperature with the abundant gaseous hydrocarbons produced by distilling wood or, in general, vegetable material. The result of such reaction between bodies of the nature just described would be to eliminate oxygen from the oily distillate by causing it to form water and carbon dioxide with the hydrogen and carbon of gaseous hydrocarbons. This idea<sup>1</sup> was confirmed by the fact that in his experiments to produce petroleum-like substances and paraffin from linseed oil Sadtler<sup>1</sup> noticed the odor of acrolein and referred to it as follows :

<sup>1</sup> Proc. Amer. Phil. Soc., 36, 93.



"At first the odor of acrolein was very pronounced and powerful, showing that the glycerine of the glycerides composing the oil was being decomposed; later the odor was more that of a cracked petroleum oil, showing that the linoleic and other acids of the oil were undergoing decomposition." On another page the same writer says, "Of course the fractions must be obtained on a sufficiently large scale to admit of thorough purifying before the character of the hydrocarbons can be studied. At present they contain impurities such as aldehyde-like and possibly ketone products. They reduce ammoniacal silver solutions and indicate thus the presence of these impurities."

The following facts based upon a consideration of the character of the distillates obtained from the mixed animal and vegetable matter, from the fish alone, and from the wood alone tend to show the correctness of the writer's position in an attempt to produce an asphalt low in oxygen. The table of ultimate analyses given below shows that there is less than half as much oxygen in the asphalt from wood and fish mixed as in that from fish alone.

*Ultimate Analyses.*

	Ash.	Carbon.	Hydrogen.	Sulphur.	Nitrogen.	Oxygen.
Utah gilsonite	0.10	85.83	10.59	0.26	2.59	0.63
Utah elaterite	....	73.49	9.46	3.17	1.90	12.37
Artificial gilsonite fr.						
wood and fish	....	86.56	7.06	0.08	1.91	4.39
Asphalt from wood	....	86.20	8.28	trace	0.29	5.23
Asphalt from fish	....	76.93	9.10	0.19	4.23	9.55

The following table giving the yields of water and oil in the various distillations is also of interest as showing the effect of water-forming reactions between hydrocarbons and oxygen compounds which doubtless took place in the hot tube through which the vapors were passed before condensation.

Material used.		Oil produced.	Water produced.
Wood.	Fish.		
Grams.	Grams.	cc.	cc.
9882	8170	3010	8240
....	4585	700	2830
4588	....	1150	890

If the wood and fish when distilled together had yielded oil and water in the same proportion as when each was distilled by itself, then there should have been a yield of 3724 cc. of oil from the mixture instead of the 3010 cc. actually produced, and instead of 8240 cc. of water there should have been only 7321 cc.

The question of the origin of asphalts is one that cannot be intelligently discussed apart from that of the origin of petroleum, or, more broadly still, apart from the origin of the bitumens in general which include natural hydrocarbons in all states of matter: solid, liquid, and gaseous. Of these three states liquid petroleum has for a variety of obvious reasons received the most attention scientifically and technologically.

The connection quite generally believed at present to exist between petroleum and the asphalts is expressed in Dana's *Mineralogy*, p. 751, as follows: "The more solid kinds graduate into the pittasphalts or mineral tar, and through these there is a gradation to petroleum. The fluid kinds change into the solid by the loss of a vaporizable portion on exposure, and also by a process of oxidation which consists first in a loss of hydrogen and finally in the oxygenation of a portion of the mass."

If it be accepted as true that petroleum and the asphalts are related, as the quotation just made would indicate, then it follows, of course, that any view as to the origin of petroleum also applies to the asphalts. A study of the literature concerning theories as to the origin of petroleum reveals a number which differ fundamentally from each other, and which are based largely upon geological evidence. It does not seem necessary here to give detailed consideration to these hypotheses in view of the thorough manner in which they have been recently summed up and reviewed by Myers, Sadtler, Peckham, Mabery, Phillips, and D. T. Day in a series of papers<sup>1</sup> read before the American Philosophical Society, February 5th, 1897. The comprehensive résumé given by Boverton Redwood in his work on *Petroleum* also contributes to make further detailed review superfluous at this time. It seems,

<sup>1</sup> *Proc. Amer. Phil. Soc.*, 36, 93.

however, that the propriety of attempting to make any one of these theories cover the entire problem of the origin of petroleum is very questionable in view of the fundamental differences in character and properties between petroleums of different sources which by the work of Schorlemmer, Warren, Mabery, Beilstein and Kurbatow, Markownikoff, Schützenberger and Jonine, Zaloziecky, and others, have been shown to exist. The following quotation from Boverton Redwood's work is of interest in this connection :

Referring to his résumé of theories he says, " From the account given in this section, it will be seen that there has been an abundance of speculation as to the origin of bitumen and that, in regard to some of the theories, a considerable amount of experimental proof has been forthcoming. Probably, on the whole, the Höfer-Engler views at present have the largest number of adherents, and in respect, at any rate, to certain descriptions of petroleum, are the most worthy of acceptance. At the same time, a careful study of the subject leads to the conclusion that some petroleum is of vegetable origin, and it therefore follows that no theory is applicable in all cases."

When we consider, for example, the striking differences in character between California petroleum and Pennsylvania petroleum to which Peckham, in a number of different papers, has earnestly called attention, the force of the last sentence quoted from Redwood will undoubtedly be keenly appreciated. Commenting upon the Höfer-Engler theory, Prof. Peckham<sup>1</sup> says, " Dr. Engler therefore considers that some change in the animal remains must have taken place in the earth, whereby all nitrogenous and other matters, save fats, were removed, the petroleum being formed from this fat alone, by the combined action of pressure and heat or by pressure only.

" In summing up the evidence as to origin, Höfer expresses the belief that petroleum is of animal origin, and has been formed without the action of excessive heat, and observes that it is found in all strata in which animal remains have been discovered.

" Combining these two statements, we arrive at this conclu-

<sup>1</sup> Proc. Amer. Phil. Soc., 36, 106.

sion as the Höfer-Engler theory, that bitumens are of animal origin, formed at low temperatures from fats alone by the combined action of pressure and heat."

"Steam is left out of this formula, and it is therefore inadequate. There is no evidence whatever that any portion of the crust of the earth has ever been subjected to the combined action of heat and pressure without the presence of steam or hot water, and, in my judgment, the steam has been a very potent factor in determining not only the formation but the transference of bitumens."

The writer, from his experience in the production of asphalts, as already described in this paper, feels like endorsing most heartily the views of Peckham in regard to the necessity of steam as a factor in the production of such asphalts, at least, as have been made the subject of experimental study.

The following is a quotation from Professor Peckham's paper on "The Genesis of Bitumens as Related to Chemical Geology,"<sup>1</sup> which sums up the most important features of his views as to the genesis of bitumens. The laboratory results which I have so far obtained seem to be quite fully in accordance with the conclusions which Prof. Peckham has reached.

"Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen; hence, when these forms accumulated in sediments which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of sediments above them up to the surface. They must also have been distilled under a gradually increasing temperature which would have been largely controlled by the pressure. While the temperature and pressure would have in every instance been the least possible, with steam always present, these physical conditions would on account of the

<sup>1</sup> *Loc. cit.*

varying porosity and consequent varying resistance of the overlying mass, have produced very great effects in some instances and very slight effects in others. As a consequence, we have in natural bitumen, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

“ If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds from marsh-gas to solid paraffine, remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances.

“ The contents of the original reservoirs borne down and invaded by heat might become involved in a second distillation at an increased pressure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitro hydrocarbon, reaching the surface under these conditions, might by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha and become finally solid asphaltum, and this through the lapse of time and abundance of material on a scale of vast magnitude.”

While it is true that most of the theories that have been advanced to explain the origin of bitumens have been directly concerned with the liquid variety ordinarily known as petroleum, and seem at least to have been based upon study, whether geological or chemical, of this variety to the exclusion of the solid form generally known as asphalt, still it is true that some theories have been advanced to explain directly the formation of asphalts aside from and independently of their possible relation to liquid petroleum.



Thus the Trinidad asphalt was looked upon by Wall<sup>1</sup> as having resulted from the gradual decomposition of vegetable matter found imbedded in it. This view is, however, no more tenable than the idea that the material originated from animal remains which have been found clearly indicated from a study of the composition of the asphalt.

When we consider the amount and the character of the strictly chemical work that has been done upon the asphalts or solid bitumens, it must be admitted that they have been decidedly neglected as compared with the liquid form. Even elementary analyses are in many cases unreliable, and there is much need of painstaking and persistent study in this field.

When we contemplate the marked differences between bitumens from different sources, it hardly seems reasonable to believe that any one theory as to the origin of these bodies can cover all the actual occurrences. It would seem that heat and pressure, singly and combined, and of various intensities acting with water both as liquid and as steam upon the same fundamental material, whether animal or vegetable, should produce a variety of carbonaceous substances differing from each other quite profoundly in physical and chemical properties. Again, similar or identical conditions prevailing with different kinds of material, whether animal or vegetable or mixtures of the two, should also yield products of various kinds. When, therefore, we consider the great possibilities of variation in combinations of natural forces, and also equally great possibilities of variation in the nature of the organic material upon which these forces may act, it is not surprising that we find as we do in various parts of the earth complicated and intimate carbonaceous mixtures, gaseous, liquid, and solid, which are usually summed up under the general name, bitumens.

The facts and figures given in this communication speak for themselves. Summed up they show that three asphaltic substances have been obtained by operations of distillation, primarily in presence of steam from natural animal and vegetable material, both separately and combined. The material obtained from the mixture of fish and wood, and called artificial

<sup>1</sup> Q. J. G. Soc., 16, 460.



gilsonite, so closely resembles the gilsonite from Utah that it is impossible, by inspection, to tell the two materials apart. The material obtained from fish alone also resembles what has been called (with questionable propriety) elaterite from Utah. While these two pairs of substances differ from each other to a greater or less extent in respect to the various parallel treatments to which they have been subjected, and while they also differ somewhat in chemical composition, as well as in solubility, specific gravity, streak, etc., these differences are all *in degree* and not in any single case *in kind*.

I am now engaged in the study of an asphalt known as nigr-ite, which occurs near the gilsonite of Utah. The differences between these two bitumens are throughout more striking than any that I have observed between the natural and the artificial substances treated of in this paper.

In conclusion, I take pleasure in acknowledging the benefit and the satisfaction I have derived from a study of the papers published by Professor Peckham, particularly the two entitled, "The Genesis of Bitumens as Related to Chemical Geology,"<sup>1</sup> and "On the Nature and Origin of Petroleum."<sup>2</sup>

I am indebted to my assistant, Mr. Eugene Leamy, for able cooperation throughout the entire work, and to one of my former pupils, Miss Georgia Porter, for the nitrogen determinations.

SWARTHMORE COLLEGE, PA.,  
February 18, 1899.

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Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

## XXII.—THE COMPOSITION OF NITROGEN IODIDE AND THE ACTION OF IODINE ON THE FATTY AMINES.

BY JAMES F. NORRIS AND ARTHUR I. FRANKLIN.

The action of the halogens on the fatty amines has been investigated by Wurtz,<sup>3</sup> Raschig,<sup>4</sup> Séliwanow,<sup>5</sup> and others. In all cases aqueous or alkaline solutions were used and the products obtained had the composition represented by the

<sup>1</sup> Proc. Amer. Phil. Soc., **37**, 108.

<sup>2</sup> *Ibid.*, **36**, 103.

<sup>3</sup> Ann. chim. phys. [3], **30**, 455.

<sup>4</sup> Ann. Chem. (Liebig), **230**, 221.

<sup>5</sup> Ber. d. chem. Ges., **25**, 3621.

formulas  $RNI_2$ ,  $R_2NI$ , etc. A short time ago Remsen and Norris<sup>1</sup> showed that compounds of a different class were formed if water was not used as a solvent, and later one of us<sup>2</sup> described more in detail the action of bromine on the fatty amines in the absence of water.

It was shown that in all cases the halogen causes the complete decomposition of a part of the amine, and that the hydrobromic acid formed unites with the rest of the amine and forms a salt. In the presence of an excess of bromine a perhalide is formed of the composition  $R_2NHBr.Br$  in the case of secondary and tertiary amines. The action of iodine on trimethylamine and dimethylamine was also described. Trimethylamine formed an addition-product of the formula  $(CH_3)_3N.I_2$ , but trimethylamine gave a perhalide,  $(CH_3)_3HN.HI.I$ , analogous to the perbromides.

The study of the action of iodine on the different classes of fatty amines has been continued, and facts have been discovered which have an important bearing on the composition of the compounds formed by the action of iodine on ammonia.

The composition of nitrogen iodide has occupied the attention of a number of chemists who have obtained markedly different results from its study. The last communication on the subject is by Chattaway,<sup>3</sup> who has reviewed the results of former workers and has studied the conditions necessary for the preparation of the compound in a pure condition. It is clearly shown that the discordant results were due to the fact that impure samples of nitrogen iodide had been investigated. As the compound cannot be crystallized and is readily decomposed by reagents, its purification is difficult. Chattaway overcame the difficulties, however, and showed that but one compound is obtained, although the method of preparation is varied. It is shown that the ratio of nitrogen to iodine is always 1 : 2, and that the compound has either the formula  $NHI_2$ , which had been previously assigned to it, or the formula  $NH_3I_2$ , which Chattaway considers the more probable from the study of its reactions. In the light of the work about to be described, the formula  $NH_3I_2$  seems improbable.

<sup>1</sup> This JOURNAL, 18, 90.

<sup>2</sup> *Ibid.*, 20, 51.

<sup>3</sup> J. Chem. Soc. (London), 69, 1572.

Before discussing the arguments of Chattaway in favor of the above formula, a summary of the results of the study of the action of iodine on the fatty amines is necessary.

It has already been stated that iodine forms a stable addition-product with trimethylamine. This compound has some reactions like those of nitrogen iodide and has the composition  $(\text{CH}_3)_3\text{N}.\text{I}_2$ , similar to that proposed by Chattaway for the iodide of nitrogen. In fact Chattaway uses the existence of this compound as an argument in favor of his conception. Dimethylamine, however, does not form such an addition-product. Iodine immediately causes substitution and the hydriodic acid formed unites with the rest of the amine and forms a salt. This difference in behavior led to a study of the action of iodine on primary, secondary, and tertiary amines in order to see if the conclusions indicated by the above facts are general.

Triethylamine was first studied. Ethereal solutions of the amine and iodine were mixed and kept at a temperature below  $-3^\circ$ . In a few minutes an oil separated, which was shown by analysis to be the periodide  $(\text{C}_2\text{H}_5)_3\text{N}.\text{HI}.\text{I}_2$ . The mother-liquor, on evaporation, gave triethylamine hydroiodide. The experiment was repeated, using carbon tetrachloride as the solvent in order to have present no hydrogen except that in the amine. The formation of the hydroiodide and periodide seemed to take place even more readily.

The action of iodine on an aqueous solution of the amine was next studied. The iodine was dissolved in a small amount of potassium iodide and was slowly added to the solution of the amine. A yellow solid separated which proved to be iodoform. When a large amount of iodine was added to a strong aqueous solution of the amine the periodide was precipitated.

It is seen, therefore, that iodine acts vigorously on triethylamine forming hydriodic acid as one of the products of decomposition. In the presence of water the decomposition goes so far that iodoform is formed. There were no indications of the formation of a simple addition-product. The substitution-product was evidently formed in small quantity and could not be isolated. The hydriodic acid produced by the reac-

tion reacted with the free amine present and converted nearly the entire amount of it into hydroiodide.

With tripropylamine the results were different. The oil formed by bringing together ethereal solutions of the amine and iodine was washed with ether, dried, and analyzed. The results showed that an addition-product of the formula  $(C_3H_7)_3N.I_2$  was formed. From the oil prismatic crystals separated after standing some weeks. These were analyzed and found to have the composition represented by the above formula. That the compound was not a periodide similar to the dimethylamine compound,  $(CH_3)_2HN.HI.I$ , was shown by its stability with concentrated sulphuric acid. The crystals were entirely unaffected by the acid, whereas the periodide decomposed instantly with liberation of hydriodic acid.

As examples of secondary amines diethylamine and diamylamine were studied. When ethereal solutions of iodine and diethylamine were mixed an oil separated, and on standing some time crystals of diethylamine hydroiodide appeared. Sulphuric acid liberated hydriodic acid from the oil which was accordingly not a simple addition-product of the amine and iodine. The amine and iodine were brought together in a carbon tetrachloride solution at  $-10^\circ$ . The hydroiodide precipitated. In aqueous solutions iodoform resulted. Analogous results were obtained when diamylamine was used. It is evident, therefore, that secondary amines do not form addition-products of the formula  $R_2HN.I_2$ . No attempt was made to isolate the substitution-product formed by the reaction since Raschig has shown that the compound  $(C_4H_9)_2NI$  is very unstable.

Methylamine was studied as a type of primary amines. Iodine caused the immediate formation of methylamine hydroiodide in ethereal or carbon tetrachloride solution.

From the above facts the conclusion is drawn that iodine readily attacks the amines, causing substitution, and that this is accompanied by the formation of an addition-product of iodine and the amine only in the case of tertiary amines. This conclusion is inconsistent with the view of Chattaway.

A number of the arguments put forward in favor of the addition-formula for nitrogen iodide receive positive answers

from the work of previous investigators on the action of iodine on the fatty amines, the work described above, and the results of experiments in progress in this laboratory on the reactions of the iodine substitution-products of the amines.

On page 1578 Chattaway (*loc. cit.*) in speaking of the action of iodine on ammonia, says, "iodine substitutes only with extraordinary difficulty, if at all, and here we have an almost instantaneous substitution, and in a group into which iodine is not known otherwise to enter." Raschig (*loc. cit.*) has shown that iodine readily reacts with methylamine in alkaline solution, forming the substitution-product,  $\text{CH}_3\text{NI}$ , and the present work shows that substitution also takes place in the absence of water.

Further, "The conclusion is again strengthened by the difference in behavior of the two elements, chlorine and iodine, towards ammonia and ammonium compounds. Nitrogen chloride is only formed when chlorine acts on an ammonium salt; as long as free ammonia is present, nitrogen is liberated. On the other hand, iodine forms nitrogen iodide only in the presence of free ammonia, and it has no substituting action on an ammonium salt, even in the presence of iodic acid." This difference in action seems to be due to the well-known difference in chemical properties of the two elements. Iodine substitutes usually, however, whenever a basic substance is acted upon as is shown by its action on aniline, by which *p*-iodoaniline is readily formed. In the presence of free ammonia substitution is possible because the hydriodic acid formed immediately unites with the ammonia and is thus removed.

Further, "One would hardly expect ammonium iodide to be formed as one of the products of its detonation if it were a substitution-product." Some experiments which will be reported in full later show that the compounds  $\text{CH}_3\text{NCl}_2$  and  $(\text{CH}_3)_2\text{NCl}$  readily decompose and give the chlorides of methylamine and dimethylamine, respectively.

And finally, "If nitrogen iodide were a substitution-derivative of ammonia, one would expect to be able by suitable reagents to replace the iodine by other groups; no such replacement, however, has ever been observed. One would expect,



for example, to be able to replace the iodine by hydroxyl by the action of water or caustic alkalies, or moist oxides of silver or lead." Attempts have been made in this laboratory to prepare tetraalkylated hydrazines by the action of silver, zinc-copper couple, and sodium on the compounds  $(\text{CH}_3)_2\text{NI}$ ,  $(\text{C}_3\text{H}_7)_2\text{NCl}$ , etc. In all cases negative results were obtained. The products formed always contained a large percentage of the amine from which the substitution-product had been obtained. Sodium thiosulphate readily decomposed iododimethylamine, but no hydrazine has yet been found. The action of silver oxide yielded mixtures from which no hydroxylamine derivative could be isolated. These results show that the decomposition of substitution-products is not simple. Experiments are still in progress on the above reactions and will be reported later.

As the reactions of nitrogen iodide do not speak positively for one formula or the other, it seems that the facts stated above are strong evidence which should be considered in deciding its formula. The action of iodine on the substituted ammonias can be more readily studied than its action on ammonia itself, and, as with the former addition-products are possible only when all the hydrogen of ammonia is replaced by alkyl groups, it seems highly probable that the compound with ammonia is not a direct addition-product.

The methods of preparation of nitrogen iodide and diiodomethylamine,  $\text{CH}_3\text{NI}_2$ , are analogous. This also speaks for the formula  $\text{NHI}_2$ .

As the work showed that the existence of a compound of the formula  $\text{NH}_2\text{I}_2$  seemed improbable, the compounds made by Guthrie<sup>1</sup> and by Seamon,<sup>2</sup> and to both of which the above formula was assigned, were prepared and studied. Guthrie prepared his compound by adding powdered iodine to a saturated solution of some easily soluble ammonium salt, partially decomposed by one-third its equivalent of potassium hydroxide. Seamon passed dry ammonia over iodine cooled by melting ice, and obtained a black oil which was not explosive.

From the work on the amines it seemed probable that a substance prepared under the above conditions would be a mix-

<sup>1</sup> J. Chem. Soc. (London), 1863, 239.

<sup>2</sup> Chem. News, 44, 188.



ture of a periodide and a substitution-product. Accordingly, ammonium periodide and the iodide of nitrogen were prepared and mixed. The periodide prepared by the method of Johnson<sup>1</sup> was a black oil. It readily dissolved large quantities of nitrogen iodide and the resulting mixture was found to have the physical properties of the compound prepared by Seamon's method.

The action of solvents on Seamon's compound and on the mixture was studied side by side. Both dissolved easily and completely in ether, although the mixture contained nearly 50 per cent of nitrogen iodide, which is insoluble in ether. Both were soluble in ethyl acetate, slightly soluble in chloroform, benzene, and carbon disulphide, and insoluble in carbon tetrachloride. When treated with water both left an explosive residue.

These facts seem to show that the action of iodine on ammonia is analogous to its action on the primary and secondary amines, and that no addition-product is formed.

In conclusion the work shows that :

1. Iodine readily attacks the fatty amines and, in the absence of water, hydroiodides and periodides are formed.
2. With some tertiary amines, addition-products of the formula  $R_3N.I_2$  are formed.
3. Nitrogen iodide is not a direct addition-product of ammonia and iodine.
4. The non-explosive substance to which the formula  $NH_3.I_2$  has been assigned is probably a mixture.

#### EXPERIMENTAL.

In all of the work to be described about molecular quantities of iodine and the amine were used, as it was thought that these conditions were the most favorable for the formation of a compound of the formula  $R_3N.I_2$ . A slight excess of the amine was present in order to avoid the presence of free iodine after the reaction.

#### *Action of Iodine on Triethylamine.*

Ethereal solutions of iodine and of triethylamine were mixed. In a few minutes an oil separated. This was

<sup>1</sup> J. Chem. Soc. (London), 33, 397.

washed with water which did not seem to affect it and was analyzed with the following results :

0.1623 gram salt gave 0.2394 gram AgI.

	Calculated for (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH.HI.I <sub>2</sub> .	Found.
I	78.88	79.73

The substance was evidently a periodide. It was not a direct addition-product as concentrated sulphuric acid caused a vigorous evolution of hydriodic acid. When the ethereal mother-liquor from the oil was evaporated more of the oil was obtained mixed with crystals of triethylamine hydroiodide, which was identified by its melting-point, 175°-176°, and by an analysis.

The experiment was repeated care being taken to keep the temperature below -3°. The same results were obtained.

Carbon tetrachloride was next used as a solvent in order to have no hydrogen present except that in the amine. An oil was formed in which white crystals of the hydroiodide appeared on standing.

A dilute aqueous solution of triethylamine was treated with iodine dissolved in potassium iodide. The yellow precipitate formed was washed and crystallized from alcohol. An analysis of the hexagonal plates which melted at 119° showed them to be iodoform.

When strong solutions of the amine and iodine were used, a red oil precipitated, an analysis of which gave results approximating those required by the formula (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N.HI.I<sub>2</sub>.

In all of the experiments there was no indication of the formation of an addition-product. No substitution-product except iodoform was isolated. Iodine probably causes the complete breaking down of a part of the amine and the hydriodic acid formed unites with the rest to form a salt.

#### *Action of Iodine on Tripropylamine.*

Ethereal solutions of the amine and of iodine when mixed formed a brown solution from which an oil separated in a few minutes. This was washed with ether and dried over sulphuric acid. After standing a few days a few red fibrous crystals, which melted at 66°, appeared. The oil was dis-

solved in alcohol and ether added; a brown crystalline precipitate was thrown down, which melted at  $59^{\circ}$ – $62^{\circ}$ . The crystals were evidently a mixture which contained some tripropylamine hydroiodide, for this compound was found in the mother-liquor from which the oil had been separated. The preparation was repeated at  $-5^{\circ}$ . The compound separated more slowly but did not come down in crystalline condition. The resulting oil, after standing two days, was washed with water. The results of an analysis agreed with the formula  $(C_3H_7)_3NH.HI.I_2$ , but there was no proof that the substance was a pure compound.

In the next experiment the oil was prepared immediately washed with ether, dried at  $90^{\circ}$ , and analyzed (Analysis I).

From the oil stout prismatic crystals separated after standing a month in a desiccator. These melted at  $66^{\circ}$  and were accordingly the same as the compound which was obtained in the first experiment. The crystals were analyzed (Analysis II).

I. 0.3208 gram salt gave 0.3687 gram AgI.

II. 0.0726 gram salt gave 0.855 gram AgI.

Calculated for $(C_3H_7)_3N.I_2$ .	I.	Found.	II.
63.98	62.12		63.64

The compound is insoluble in ether, slightly soluble in carbon tetrachloride, soluble in ethyl acetate and chloroform. With water the crystals melt to an oil. Concentrated sulphuric acid had no action on them. The compound was therefore not a periodide.

When carbon tetrachloride was used as solvent for the amine and iodine, the oil was formed as well as a large amount of tripropylamine hydroiodide.

In aqueous solution iodine dissolved in potassium iodide precipitated an oil which gave results on analysis agreeing with the formula of the periodide  $(C_3H_7)_3N.HI.I_2$ .

#### *Action of Iodine on Diethylamine.*

When ethereal solutions of the amine and iodine were mixed a dark oil precipitated, and, after standing some time, crystals of diethylamine hydroiodide were formed in the solu-

tion. Concentrated sulphuric acid set free hydriodic acid from the oil which was accordingly not a simple addition-product of the amine and iodine. The same result was obtained when the solutions were kept at  $-5^{\circ}$ , except that the oil separated more slowly.

When carbon tetrachloride was used as the solvent and iodine was added to the amine, a white crystalline precipitate of the hydroiodide of the amine appeared immediately. This was changed by the addition of more iodine, to a periodide, a dark-brown crystalline precipitate, which melted to an oil when brought in contact with the air. At  $-10^{\circ}$  the result was the same.

In dilute aqueous solution, in the presence of sodium carbonate, iodoform was formed.

The action of iodine on the amine, without the presence of a solvent, was also investigated. At the ordinary temperature the action was violent and was accompanied by much heat and the evolution of white fumes. At  $-18^{\circ}$  the two substances were inactive.

No addition-product was found as the result of the action of the two substances on each other. Under all circumstances the reaction resulted in the formation of a large amount of diethylamine hydroiodide, showing that iodine had caused substitution.

#### *Action of Iodine on Diamylamine.*

Solutions of the amine and of iodine in ether were mixed. The temperature rose and a black crystalline salt precipitated. This was washed with ether and analyzed.

I. 0.4320 gram salt gave 0.5692 gram AgI.

II. 0.3811 gram salt gave 0.5019 gram AgI.

Calculated for (C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> NH.HI.I <sub>2</sub> .	I.	Found. II.
70.68	71.12	71.25

The periodide prepared from the hydroiodide and iodine dissolved in hydriodic acid had the appearance and properties of the salt prepared as above.

Solutions which had been cooled in a freezing-mixture were next mixed. After standing some time, diamylamine hydro-

iodide crystallized out. From the mother-liquor a dark oil separated which had the properties of periodide.

*Action of Iodine on Methylamine.*

Dry methylamine was passed into an ethereal solution of iodine ; a black crystalline precipitate was formed which was shown by analysis to be a periodide.

As in this experiment the iodine was in excess, a solution of iodine in carbon tetrachloride was added to a solution of the amine in the same solvent. Methylamine hydroiodide separated immediately. No addition product of the amine was formed.

*Action of Iodine on Ammonia.*

The experiment of Seamon<sup>1</sup> was repeated. Dry ammonia was passed over iodine in a flask surrounded by ice. The reaction-product was a black oil which contained a small amount of a solid which was explosive when washed with ether. The oil was not explosive, however, and had the properties assigned to it by Seamon. It was soluble in ether and ethyl acetate, less soluble in chloroform, benzene, and carbon disulphide, and insoluble in carbon tetrachloride. Water decomposed it and nitrogen iodide was formed.

The substance prepared by Guthrie's<sup>2</sup> method was a greenish-black, thick liquid, which resembled the above compound closely.

As it seemed probable that compounds prepared as above would contain ammonium periodide and nitrogen iodide these substances were made and mixed. Ammonium periodide made according to Johnson was a black, heavy liquid. It readily dissolved nitrogen iodide, and the resulting mixture had all the properties of the substances described above. The mixture dissolved readily in ether, although nitrogen iodide is insoluble in this solvent.

BOSTON, MASS., February, 1899.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

# CXII.—ON THE ACTION OF SODIC ETHYLATE ON TRIBROMDINITROBENZOL.<sup>1</sup>

BY C. LORING JACKSON AND WALDEMAR KOCH.

The principal object of the work described in this paper was to determine the constitution of the dinitroresorcine diethylether melting at 133°, formed by the action of a hot solution of sodic ethylate on tribromdinitrobenzol, (Br,<sub>3</sub>1,3,5,(NO<sub>2</sub>)<sub>2</sub>,4), or on the bromdinitroresorcine diethylether melting at 184°. This determination was of interest to us, as it formed part of an investigation of the replacement of bromine by hydrogen under the influence of sodium malonic ester, sodic ethylate, and similar reagents, which has now been in progress for several years in this laboratory. In all the cases studied here, with a single exception, the atom of bromine (or iodine) has stood between two radicals, each in the ortho position to it and it was necessary to determine whether this arrangement also existed in this case, since a consideration of the possibilities shows that this dinitroresorcine diethylether might have either the symmetrical structure, if the bromine between the two nitro groups was replaced by hydrogen, or the adjacent structure, if this replacement occurred with one of the other atoms of bromine.

The constitution of the diethylether was determined by saponifying it to the corresponding dinitroresorcine, which proved to be the symmetrical compound, (OH)<sub>2</sub>1,5(NO<sub>2</sub>)<sub>2</sub>,4, melting at 212°.5, according to Typke.<sup>2</sup> The proof that this body has the structure assigned to it has been given by Nietzki and Schmidt,<sup>3</sup> who converted it into diimidoresorcine, which in turn yielded dioxyquinone by treatment with sodic hydrate, and this dioxyquinone gave with nitric acid nitranilic acid, which is paradinitrodioxyquinone, a result that is in harmony only with the symmetrical structure for the dinitroresorcine. It follows therefore that the bromine replaced by hydrogen in tribromdinitrobenzol is the one between the two nitro groups, as we had expected from the results of pre-

<sup>1</sup> Presented to the American Academy of Arts and Sciences, Oct. 12, 1898.

<sup>2</sup> Ber. d. chem. Ges., 16, 552.

<sup>3</sup> *Ibid.*, 21, 2374.



vious experiments, and that the bromdinitroresorcine diethylether melting at  $184^{\circ}$  has the constitution  $(OC_2H_5)_{1,5}, Br3.(NO_2)_{2,4}$ . It is an interesting fact in this connection that an isomeric bromdinitroresorcine diethylether (having the constitution  $(OC_2H_5)_{1,3}, Br5.(NO_2)_{2,4}$ ), in which the bromine is not in the ortho position to two nitro groups, gave no replacement of the atom of bromine by hydrogen, but, when treated with sodic ethylate, gave dinitrophenylglucine triethylether by the replacement of the bromine by an ethoxy group. Beilstein, in the third edition of his *Handbuch*, provisionally places the diethylether,  $C_6H_2(OC_2H_5)_2(NO_2)_2$ , melting at  $133^{\circ}$ , and the corresponding dimethylether,  $C_6H_2(OCH_3)_2(NO_2)_2$ , melting at  $167^{\circ}$ , prepared from tribromdinitrobenzol by W. H. Warren and one of us,<sup>1</sup> under the adjacent dinitroresorcine. The determination of the constitution of the diethylether just given necessitates their transfer to the symmetrical dinitroresorcine, as there can be no question that the methylether has the same structure as the ethyl compound. It also shows that the dimethylether,  $C_6H_2(OCH_3)_2(NO_2)_2$ , melting at  $67^{\circ}$ , prepared by Hönig<sup>2</sup> by the direct action of nitric acid on a solution of resorcine dimethylether in glacial acetic acid, cannot have the symmetrical structure which Beilstein assigned to it, as this now belongs to the body melting at  $167^{\circ}$ .

In addition to this determination of the constitution of dinitroresorcine diethylether, we have made a more careful study of the products of the reaction between sodic ethylate and tribromdinitrobenzol melting at  $192^{\circ}$  both at ordinary temperatures and when aided by heat. These reactions had already been studied by W. H. Warren and one of us,<sup>3</sup> with the result that in the cold the bromdinitroresorcine diethylether melting at  $184^{\circ}$  was formed, whereas, when hot, the dinitroresorcine diethylether melting at  $133^{\circ}$  was the product isolated. As, however, subsequent work<sup>4</sup> upon the tribromtrinitrobenzol showed that in that case the action was far from simple, it hardly seemed probable that the dinitro compound had given only one organic product in each of these cases, and this inference was confirmed by our first new ex-

<sup>1</sup> This JOURNAL, 13, 170, 179.

<sup>2</sup> Ber. d. chem. Ges., 11, 1041.

<sup>3</sup> This JOURNAL, 13, 167.

<sup>4</sup> Jackson and Warren: *Ibid.*, 15, 607.

periment in this field, as we found sodic nitrite as well as sodic bromide among the products of the reaction, so that it was evident that some other compounds were present beside those recognized by Warren and one of us. The result of this later work was the isolation of the following products of the action of sodic ethylate on tribromdinitrobenzol, melting-point  $192^{\circ}$ , when absolute alcohol and benzol are used as the solvents, and the mixture is allowed to stand at ordinary temperatures:

(1) Bromdinitroresorcine diethylether,  $C_6HBr(OC_2H_5)_2(NO_2)_2$ , melting at  $184^{\circ}$ ,  $(OC_2H_5)_2$ , 1,5,  $Br_3(NO_2)_2$ , 2,4.

(2) Bromdinitroresorcine diethylether,  $C_6HBr(OC_2H_5)_2(NO_2)_2$ , melting at  $92^{\circ}$ ,  $(OC_2H_5)_2$ , 1,3,  $Br_5(NO_2)_2$ , 2,4.

(3) Tribromnitrophenol,  $C_6HBr_3(NO_2)OH$ , melting at  $90^{\circ}$ ,  $Br_3$ , 1,3,5,  $NO_2$ , 2,  $OH_4$ .

(4) Dinitroresorcine monoethylether,  $C_6H_2(OC_2H_5)OH(NO_2)_2$ , melting at  $77^{\circ}$ ,  $(OC_2H_5)$ , 1,  $OH_5$ ,  $(NO_2)_2$ , 2,4.

(5) Dinitrophloroglucine triethylether,  $C_6H(OC_2H_5)_3(NO_2)_2$ , melting at  $105^{\circ}$ ,  $(OC_2H_5)_3$ , 1,3,5,  $(NO_2)_2$ , 2,4.

These products indicate that there are three primary reactions, when sodic ethylate acts on tribromdinitrobenzol. These are, Reactions I. and II., consisting in the replacement of two atoms of bromine by two ethoxy groups, producing the two isomeric bromdinitroresorcine diethylethers (1) and (2), and Reaction III., in which one nitro group is replaced by one hydroxyl group (or by an ethoxy group followed by saponification) giving the tribromnitrophenyl (3). There are also two secondary reactions owing to the further action of sodic ethylate on the products of Reactions I. and II.; first, the replacement of the bromine in the bromdinitroresorcine diethylether (1) by an atom of hydrogen (followed by partial saponification) giving the dinitroresorcine monoethylether (4); and secondly, the replacement of the bromine in the bromdinitroresorcine diethylether (2) by the ethoxy group, giving the dinitrophloroglucine triethylether (5). The saponification mentioned in this paragraph might be brought about by the sodic hydrate formed from the sodic ethylate by the water added in the course of the purification, but it seems to us more probable that the phenols were formed by some

sodic hydrate acting directly on the tribromdinitrobenzol, since the ethers of the phenols seemed decidedly stable, when treated with an alkali.

The following estimations of the approximate yields of the products give a rough idea of the extent to which each of the three primary reactions ran :

	Per cent.
Reaction I., forming substances (1) and (4)	28
Reaction II., forming substances (2) and (5)	38
Reaction III., forming substance (3)	1
Total	67

As most of these substances were purified by crystallization, too much weight must not be given to these yields, but we can safely infer from them that Reaction II. ran to the largest extent, Reaction I. came next, and Reaction III. took place only to a very limited extent.

These results are capable of a satisfactory theoretical explanation, but before giving this it will be well to consider a parallel case studied by W. H. Warren and one of us,<sup>1</sup> in which the conditions are simpler and rather better marked. This is the action of sodic ethylate on symmetrical tribromtrinitrobenzol,  $C_6Br_3(NO_2)_3$  (Br, 1, 3, 5,  $(NO_2)_3$ , 2, 4, 6) which consisted of two simultaneous reactions, first, the replacement of two nitro groups by two ethoxy groups, giving  $C_6Br_3NO_2(OC_2H_5)_2$ , and second, the replacement of the three bromine atoms by three ethoxy groups, giving  $C_6(C_2H_5)_3(NO_2)_3$ . These two reactions ran to nearly an equal extent (about 45 per cent of each product), if the solvent was alcohol only.<sup>2</sup> In attempting to explain these experimental results we must consider the agencies which tend to loosen the nitro groups on the one hand and the atoms of bromine on the other from the benzol ring. We have designated these agencies by letters, and arranged them in the order of intensity, beginning with the strongest.

A. The loosening effect of the three nitro groups on the three atoms of bromine. This is a strong agency, as shown

<sup>1</sup> This JOURNAL, 15, 619.

<sup>2</sup> If the solvent was benzol and alcohol, less of the nitro groups were replaced; but this case need not be considered in this discussion.

by the fact that picryl chloride (in which the chlorine is similarly disposed to the three nitro groups) is decomposed easily and completely, even at ordinary temperatures.<sup>1</sup>

*B.* The loosening effect exerted by the three nitro groups on each other. Lobry de Bruyn<sup>2</sup> has shown that symmetrical trinitrobenzol is converted into dinitroanisol by sodic methylate, even at ordinary temperatures; this loosening effect is therefore a powerful one, but not quite so strong as *A*, since the action of picryl chloride is complete in a few minutes, whereas the reaction with trinitrobenzol needs several days, if carried on in the cold.

*C.* The loosening effect of the three atoms of bromine on the three nitro groups. This is a much weaker action than *B*, since with the tetrabrombenzol,<sup>3</sup> ( $\text{Br}_{4,1,2,4,6}$ ), the atom of bromine (which stands in the same position toward the three atoms of bromine as the three nitro groups do in our compound) was removed only after long boiling of the benzol and alcohol solution with sodic alcoholate, and then incompletely.

*D.* The loosening effect of the three bromine atoms on each other. This is a feeble effect, as Blau<sup>4</sup> found it necessary to heat symmetrical tribrombenzol to  $120^{\circ}$ – $130^{\circ}$  with sodic methylate to obtain much action. Calvert and one of us<sup>5</sup> found that with sodic ethylate a reaction took place at the boiling-point of alcohol in open vessels, but the reaction ran more slowly, and was less complete than that with tetrabrombenzol.

We have then the most powerful loosening effect *A*, and the weakest loosening effect *D*, exerted on the atoms of bromine, while the two intermediate effects *B* and *C* influence the nitro groups, so that  $A + D$  is very nearly, if not quite, equal to  $B + C$ ; that is, the attack of the sodic ethylate will be directed about equally upon the atoms of bromine and upon the nitro groups, which was the result of our experimental work as stated above.

A similar discussion of the action of sodic ethylate on tribromdinitrobenzol gives the following results. The loosening effects are marked by letter, and arranged in order of intensity as before.

<sup>1</sup> This JOURNAL, 20, 447.

<sup>2</sup> Rec. Trav. Chim. Pays-Bas., 9, 208.

<sup>3</sup> Jackson and Calvert: This JOURNAL, 18, 309.

<sup>4</sup> Monatsh. f. Chem., 7, 630.

<sup>5</sup> This JOURNAL, 18, 310.

*E.* The action of the two nitro groups in loosening the three atoms of bromine. This is a strong effect, as shown by the ease with which the bromdinitrobenzol,  $\text{BrI}(\text{NO}_2)_{2,4}$ , is decomposed by potassic hydrate.<sup>1</sup>

*F.* The effect of the three atoms of bromine on the two nitro-groups already discussed.

*G.* The effect of the three atoms of bromine on one another, which has also been considered in the previous discussion.

*H.* The effect of the two nitro groups on each other. So far as we can find, this effect is too feeble to produce a replacement of the nitro group by an ethoxy group, but it should not be left out of account, as Lobry de Bruyn<sup>2</sup> has found that potassic cyanide in alcoholic solution converts metadinitrobenzol into  $\text{C}_6\text{H}_3\text{NO}_2\text{OC}_2\text{H}_5\text{CN}$ , which shows a certain loosening of one of the nitro groups.

Here then we have only one strong loosening agency (*E*), and this acts on the atoms of bromine, while of the other three by far the feeblest (*H*) is one of those acting on the nitro groups. It is evident therefore that

$$E + G > F + H,$$

or, putting it into words, the attack upon the nitro groups will be insignificant compared to that on the atoms of bromine. This is in accord with our experimental results already given, since the attack on the nitro groups (Reaction III.) was to the attack on the atoms of bromine (Reactions I. and II.) as 1 to 66.

From the yields of the two bromdinitroresorcine diethylethers, given earlier in this paper, it is possible to draw conclusions in regard to the effect of the position of the nitro groups in loosening the atoms of bromine, but there is some question whether such conclusions are valid, since the difference between the yields of the two bromdinitroresorcine diethylethers is only ten per cent, and this amount is within the probable limit of error in this case, where the purifications were made by crystallization. On the other hand, the product melting at  $92^\circ$  (2) was obtained in the larger quantity, and this is the one where we should expect the greatest loss,

<sup>1</sup> Clemm : Jour. Pr. Chem., [2], 1, 145.

<sup>2</sup> Rec. Trav. Chim. Pays-Bas, 2, 205.



since in its purification the crystallizations were the most numerous. We feel, therefore, justified in giving the following discussion with all necessary reserve. In the two reactions (I. and II.) one of the atoms of bromine replaced occupied in each case the same position (ortho-para) toward the nitro groups, and therefore the difference between the reactions depends on the position of the second atom of bromine replaced. In Reaction I. this atom of bromine was ortho to one nitro group and para to the other, and this reaction gave 28 per cent of the product compared to 38 per cent from Reaction II., in which the atom of bromine was in the ortho position to both nitro groups. It would seem therefore, that the diortho position of the nitro groups exerted a stronger loosening effect upon the bromine than the orthopara position.

When the reaction between tribromdinitrobenzol and sodic ethylate is carried on at  $70^{\circ}$ , the products isolated by us were the dinitroresorcine diethylether melting at  $133^{\circ}$ , a little of the bromdinitroresorcine diethylether melting at  $184^{\circ}$ , and much of the isomeric substance melting at  $92^{\circ}$ . These were the only products we have succeeded in identifying, although we obtained indications of the presence of the tribromnitrophenol. There was also a crystalline substance melting at  $212^{\circ}$ , but in too small quantity for identification, and a great deal of tarry matter. The absence of the dinitrophloroglucine triethylether is surprising; we should account for it by supposing that the reaction ran for so short a time (ten minutes) that the bromdinitroresorcine melting at  $92^{\circ}$  did not undergo decomposition. The hypothesis that the phloroglucine ether formed was converted into tarry substances by the hot sodic ethylate seems to us less probable. The approximate yields of the two products of the reaction at  $70^{\circ}$  were :

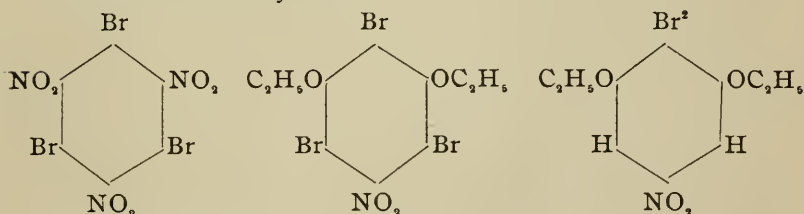
	Per cent.
Dinitroresorcine diethylether, melting-point $133^{\circ}$	16
Bromdinitroresorcine diethylether, melting-point $92^{\circ}$	9
	<hr/>
Total	25

So that in this case 75 per cent of the substance was unaccounted for. Most of this undoubtedly went into the tarry products.



The most striking phenomenon in the action of sodic ethylate on tribromdinitrobenzol at high temperatures is the replacement of hydrogen of the atom of bromine in the ortho position to both nitro groups. The fact that this reaction only takes place to a very limited extent in the cold may perhaps be accounted for by the sparing solubility of the bromdinitroresorcine diethylether melting at  $184^{\circ}$  in the cold alcohol and benzol, so that most of it is precipitated, and therefore removed from the action of the ethylate. On the other hand, as this ether is easily soluble in these liquids, when hot, it would be brought into the sphere of the reaction under these conditions, and the dinitroresorcine diethylether would be formed. The bromdinitroresorcine diethylether melting at  $92^{\circ}$  is soluble in the cold solvents, and this probably accounts for the fact that a considerable amount of it was converted into the dinitrophloroglucine triethylether even in the cold.

It is perhaps worth while to call attention to the fact that in the reactions described in this paper the action is confined either to the atoms of bromine or to the nitro groups; that is, if it has started in one set of radicals in the meta position to each other, it does not extend to the other set of radicals in the meta position to each other and ortho or para to the first set. This observation has been made frequently in the course of the investigation of which this is a part, and the principle has sometimes given valuable aid in interpreting experimental results. In only a single case has such an extension of the reaction beyond the limits of the first set of trimeta positions been observed; this was in the action of hot sodic ethylate on tribromtrinitrobenzol,<sup>1</sup> which gave first tribromnitroresorcine diethylether, and by further action bromnitroresorcine diethylether



<sup>1</sup> This JOURNAL, 15, 640.

<sup>2</sup> The position of the atom of bromine in this substance has not been established experimentally.

We are not, however, inclined to be too sure of the general occurrence of this restriction of reactions to a single trimeta zone, since the exceptional action just mentioned, in which the second trimeta zone was invaded, was accompanied by the formation of much tarry matter, and therefore it is possible that the tarry products so frequent in these reactions may have been formed by similar invasions of the second trimeta zone. The bearing of these observations on the benzol formula of J. N. Collie<sup>1</sup> is obvious.

*Preparation of Symmetrical Tribromdinitrobenzol.*

The description of the preparation of tribromdinitrobenzol is scattered through a number of papers from this laboratory, so that it would be a matter of some difficulty to find it, and there would be danger that anyone looking it up might not find the latest and best form of the process; we have thought it well, therefore, to give here a connected account of this process.

To make tribromaniline, 60 grams of aniline were treated with dilute hydrochloric acid, and dissolved in four liters of water. Then a rapid stream of air saturated with bromine vapor was drawn through the liquid by means of a Bunsen pump, until it assumed a distinct yellow color, which did not change for several minutes. The amount of bromine required was about 320 grams. The precipitate of tribromaniline was filtered out through cheese-cloth, washed until free from acid and dried by pressing with a screw press, followed by heating to about 60° over a steam radiator.

To convert this tribromaniline into tribrombenzol, 100 grams of it were dissolved in 600 cc. of alcohol and 150 cc. of benzol by the aid of heat; 40 cc. of common strong sulphuric acid were then added to the hot solution from a pipette, and any precipitate formed was dissolved by longer heating, or even adding more of the solvents. Forty grams of finely powdered sodic nitrite were next sifted into the hot solution as rapidly as the violence of the reaction permitted, and the product heated, until there was no more effervescence, after which it was allowed to stand at ordinary temperatures over night, and then filtered and dried.

<sup>1</sup> Proc. Chem. Soc., 1896-1897, p. 143.

The tribrombenzol was converted into tribromdinitrobenzol as follows: The perfectly dry tribrombenzol was mixed with four or five times its weight of fuming nitric acid of specific gravity 1.51, and gently heated over a low flame for two hours in a flask closed with a porcelain crucible, taking care that the temperature was kept just below boiling. It was then allowed to stand over night at ordinary temperatures, when most of the tribromdinitrobenzol crystallized out, while the rest of it was obtained by pouring the supernatant acid liquid into a large excess of water. The dried product was purified by crystallization from about eight times its weight of a mixture of three parts of alcohol with one of benzol.

*Action of Sodid Ethylate on Tribromdinitrobenzol at 70°.*

The tribromdinitrobenzol used in all this work, made in the way described in the previous section, melted at 192°, and had the constitution  $\text{Br}_{1,3,5}, (\text{NO}_2)_{2,4}$ . Forty grams of this tribromdinitrobenzol were dissolved in 80 cc. of benzol, and mixed with the solution of sodic ethylate obtained from 6.8 grams of sodium and 180 cc. of absolute alcohol, which gave the proportion of three molecules of sodic ethylate to each molecule of tribromdinitrobenzol. The flask containing the mixture was then placed in a water-bath, which was heated until a thermometer immersed in the mixture rose to 70°, at which temperature the solution was kept for ten minutes. The liquid turned dark brown during this heating, a color which had been found to be characteristic of the reaction with the aid of heat. At the end of the ten minutes the liquid was poured into a large evaporating dish, and the solvents allowed to evaporate spontaneously. The residue thus obtained was washed with water until the wash-water became colorless, and the product purified as follows.

*Residue Insoluble in Water.*

This residue was dried and extracted three times with boiling ligroin. The portion insoluble in ligroin was purified by repeated crystallization from a mixture of ligroin and benzol, during which it was frequently treated with bone-black. The product was the dinitroresorcine diethylether already ob-

tained in this way by W. H. Warren and one of us; <sup>1</sup> it was recognized by its melting-point, 133°, and its solubilities and appearance.

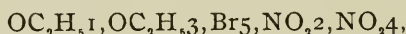
The ligroin solution on standing deposited a flocculent precipitate in too small quantity for identification, which was filtered out, and the filtrate evaporated to dryness; the crystalline residue was spread on an unglazed plate to remove oily impurities, after which it was purified by crystallization from hot ligroin. After four crystallizations it showed the constant melting-point 92°, when it was dried *in vacuo*, and analyzed with the following result:

I. 0.2043 gram of the substance gave by the method of Carius 0.1136 gram of argentic bromide.

II. 0.2885 gram of the substance gave 20.6 cc. of nitrogen at a temperature of 12° and a pressure of 745 mm.

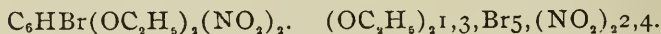
	Calculated for $C_6HBr(OC_2H_5)_2(NO_2)_2$ .	I.	Found. II.
Bromine	23.89	23.69	....
Nitrogen	8.36	....	8.32

The substance is therefore a bromdinitroresorcine diethylether isomeric with the one obtained by W. H. Warren and one of us<sup>2</sup> by the action of cold sodic ethylate upon the tribromdinitrobenzol and melting at 184°. As the constitution of this substance has been established (in this paper) as  $OC_2H_5I, OC_2H_5, Br_3, NO_2, NO_4$ , it follows that our new bromdinitroresorcine diethylether must have the constitution



as this is the only other body with this composition which can be obtained from the tribromdinitrobenzol.

*Properties of Bromdinitroresorcine Diethylether. Melting-point 92°.*



This substance crystallizes in white needles thickly crowded into bunches shaped like hour-glasses; when better developed, they form prisms with blunt ends, which seem to be made up of a basal plane modified by very minute planes of a pyramid. On long exposure to the air, especially in bright light, it

<sup>1</sup> This JOURNAL, 13, 170.

<sup>2</sup> Ibid., 13, 167.

turns brownish, and this change is accompanied by decomposition. It melts at  $92^{\circ}$ ; and is freely soluble even in the cold in benzol, ether, chloroform, acetone, glacial acetic acid, carbonic disulphide, or acetic ester; somewhat soluble in cold alcohol, freely in hot; sparingly soluble in cold ligroin, freely in hot; essentially insoluble in water whether cold or hot. Ligroin is the best solvent for it. A hot solution of sodic hydrate has little or no action on it. On heating it with sodic ethylate it is converted almost quantitatively into the triethylether of dinitrophloroglucine formed by the replacement of its atom of bromine by an ethoxy group; the product was recognized by its melting-point,  $105^{\circ}$ , and its other properties. The wash waters gave no test for a nitrite, showing that the nitro groups had not been attacked.

*Other Products of the Reaction.*—During the purification of the dinitroresorcine diethylether a small quantity of the bromdinitroresorcine diethylether melting at  $184^{\circ}$  was isolated. Its presence shows that the heating for ten minutes used by us was not sufficient to convert the whole of it into the dinitroresorcine diethylether.

From the ligroin mother-liquors of the bromdinitroresorcine diethylether melting at  $92^{\circ}$ , a few milligrams of a body were obtained, which melted constant at  $112^{\circ}$ , contained bromine, and gave no test for nitrogen after fusion with sodium.<sup>1</sup> We supposed, therefore, that we had the tribromresorcine, which melts according to Benedikt at  $111^{\circ}$ , and could be formed by the replacement of the two nitro groups by ethoxy radicals, followed by saponification; but upon comparing our specimen with some tribromresorcine made for this purpose, it was found that, although the two substances melted at the same point, (as we found the melting-point  $112^{\circ}$ – $113^{\circ}$  for the tribromresorcine), they differed markedly in solubility in alcohol, our substance being much less soluble, and also in the method of crystallization, although the forms were not incompatible. That our substance was not tribromresorcine was proved by the action of sodic hydrate, which did not affect our body, whereas it dissolved the tribromresorcine instantly, giving a solution which turned black almost at once.

<sup>1</sup> We do not feel that this proves the substance is free from nitrogen.



The amount of our substance was not enough for analysis, so we can make no statement in regard to its nature. We add a description of its crystalline form, which may lead to its identification. It forms when crystallized from alcohol white very sharp needles, which when better developed appear as slender prisms with square ends or bluntly sharpened by several planes at very obtuse angles to the sides and terminated by a basal plane. When less well developed, it forms felted masses of needles or bunches, or long sheaves of needles. None of the arborescent forms were observed which seemed to be characteristic of the tribromresorcine. This substance was also characterized by its solubility in ligroin. It was only formed in very minute quantities under the conditions of the reaction used by us.

*The Products of the Reaction Soluble in Water.*

The wash-waters obtained from the product of the action of sodic ethylate on tribromdinitrobenzol at  $70^{\circ}$  were highly colored, but the substances obtained by acidifying them with acetic acid were so tarry that we could not isolate any body fit for analysis. The filtrate from this tar, which was also colored, was evaporated to small bulk, and treated with baric chloride, when a gelatinous precipitate was obtained, which resembled the barium salt of tribromnitrophenol described later in this paper. We did not, however, succeed in getting enough of it to purify for analysis.

The approximate yields of the principal products of the action of sodic ethylate on tribromdinitrobenzol at  $70^{\circ}$  were determined as follows :

	Per cent.
Dinitroresorcine diethylether	16
Bromdinitroresorcine diethylether melting at $92^{\circ}$	9
	<hr/>
Total	25

From which it appears that 75 per cent of the theoretical yield had been converted into the tarry mass, from which we could isolate nothing fit for analysis.

*Action of Sodic Ethylate upon Tribromdinitrobenzol in the Cold.*

The proportions used were the same as those used in the



experiment at 70°, that is, 40 grams of the tribromdinitrobenzol dissolved in 80 cc. of benzol and mixed with the sodic ethylate from 6.8 grams of sodium and 180 cc. of absolute alcohol. The mixture was allowed to stand in a corked flask from three to five days with frequent shaking, after which it was poured into an evaporating dish, and allowed to evaporate spontaneously. The residue was washed with water until the washings were colorless, and the products were then purified as follows.

*Residue Insoluble in Water.*

This was dried and extracted three times with boiling ligroin, which left a crystalline residue, and this after recrystallization from a mixture of alcohol and benzol showed the constant melting-point 184°, and was therefore the bromdinitroresorcine diethylether discovered by W. H. Warren and one of us in the previous work on this reaction.

The ligroin extract was allowed to stand over night, when it deposited crystals, which were filtered out, and strangely enough proved to be essentially insoluble in ligroin. As they could not have been formed in the ligroin solution, we can explain the extraction of them by hot ligroin only by supposing they are soluble in a mixture of ligroin and the other (soluble) product of the reaction. The crystals after purification by crystallization from a mixture of alcohol and benzol showed the constant melting-point 105°, which suggested that they were the dinitrophloroglucine triethylether discovered by W. R. Lamar and one of us.<sup>1</sup> To settle the nature of the substance, it was dried at 100° and analyzed with the following result:

0.2297 gram of the substance gave 19.4 cc. of nitrogen at a temperature of 23° and a pressure of 750 mm.

	Calculated for $C_6H(OC_2H_5)_3(NO_2)_2$ .	Found.
Nitrogen	9.34	9.42

It is therefore the dinitrophloroglucine triethylether.

The ligroin mother-liquor, from which the dinitrophloroglucine triethylether had been deposited, was evaporated to dryness, and spread on a porous plate to remove oily impuri-

<sup>1</sup> This JOURNAL, 18, 670.

ties, after which it was dissolved in hot ligroin and allowed to crystallize, when in addition to the square prisms of dinitrophloroglucine triethylether long needles with square ends were observed, which resembled the bromdinitroresorcine diethylether melting at  $92^{\circ}$ , obtained by the action of a hot sodic ethylate solution on tribromdinitrobenzol, as described earlier in this paper. The isolation of this substance from the mixture of crystals proved a matter of great difficulty. Hot ligroin did not accomplish this, and a number of other solvents were tried with no better results. Finally, on soaking the mixture for some time with cold ligroin, it was found that a considerable amount of the square prisms remained undissolved; these were filtered out, and the filtrate on evaporation gave a residue, which was once more extracted with cold ligroin in the same way. The second extract yielded crystals, which could be purified by crystallization from hot ligroin, when their constant melting-point,  $92^{\circ}$ , and their solubilities and crystalline form proved that they were the bromdinitroresorcine diethylether  $(OC_2H_5)_2I_3Br_5(NO_2)_{2,4}$ .

Although the dinitrophloroglucine triethylether was formed freely in the cold, we obtained none of it when we carried on the reaction at  $70^{\circ}$ . This was probably due to the short duration of our experiments (ten minutes), as there is little doubt that this substance is produced by the further action of the sodic ethylate on the bromdinitroresorcine diethylether at first formed. It follows that the best way of making the diethylether melting at  $92^{\circ}$  is the process described under the action of sodic ethylate at  $70^{\circ}$ .

*Products of the Reaction Soluble in Water.*

The first step in purifying the products of the reaction of sodic ethylate on tribromdinitrobenzol in the cold consisted in washing with water; the highly colored wash-waters were concentrated and acidified with acetic acid, which produced a flocculent precipitate; this was dissolved in dilute alcohol, filtered, and the hot filtrate treated with an aqueous solution of baric hydrate. On cooling, beautiful, leaf-like, lemon-yellow crystals of a barium salt separated, which, after purifica-

tion by recrystallizing from water, were dried at 100°, and the barium determined with the following result :

0.3916 gram salt gave 0.1446 gram of baric sulphate.

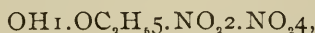
	Calculated for $[\text{C}_6\text{H}_2(\text{OC}_2\text{H}_5)(\text{NO}_2)_2\text{O}]_2\text{Ba}_2\text{H}_2\text{O}$ .	Found.
Barium	21.78	21.71

The retention of the two molecules of water at 100° is certainly strange, especially as the salt changed from lemon-yellow to orange on heating, evidently from loss of water, and, as therefore this analysis was not sufficient to establish the identity of the substance, we prepared the free phenol by decomposing the barium salt with acetic acid. It was recrystallized from alcohol, until it showed the constant melting-point 77°, when it was dried *in vacuo*, and analyzed with the following result :

0.2125 gram of the substance gave 22.1 cc. of nitrogen at a temperature of 15° and a pressure of 752 mm.

	Calculated for $\text{C}_6\text{H}_2\text{OHOC}_2\text{H}_5(\text{NO}_2)_2$ .	Found.
Nitrogen	12.28	12.11

The body is therefore a dinitroresorcine monoethylether, and seems to be identical with that discovered by Aronheim<sup>1</sup> by treating nitrosoresorcine ethylether with nitric acid, as the descriptions of the appearance and solubilities of the two bodies coincide, but Aronheim gives the melting-point 75°, whereas we found 77°. It seemed necessary therefore to establish the identity of our body more firmly, and this was done by saponifying a specimen of it by boiling for half an hour with a sulphuric acid of specific gravity 1.44. As the dinitroresorcine thus obtained melted at 212°, our body has the symmetrical structure



and is the monoethylether corresponding to the diethylether formed by the action of hot sodic ethylate on tribromdinitrobenzol (see later in this paper). Whether our substance is identical with that discovered by Aronheim, or the difference of two degrees in the melting-point is caused by a difference in constitution, we are unable to determine with our present knowledge.

<sup>1</sup> Ber. d. chem. Ges., 12, 32.

The filtrate, from which the dinitroresorcine monoethyl-ether had been precipitated by acetic acid, still contained a phenol to judge by its color, and to obtain this hydrochloric acid was added, which produced a white precipitate. Without filtering, the liquid was extracted with ether, and, as this removed almost all of the color, the aqueous liquid was thrown away. The ether on evaporation usually left a red oily mass, which obstinately refused to crystallize; on one occasion, however, we succeeded in obtaining about half a gram of a solid, which after recrystallization from alcohol showed the constant melting-point  $90^{\circ}$ , and agreed in its properties with those described for the tribromnitrophenol, which melts at  $89^{\circ}$  according to Dacomo.<sup>1</sup> To characterize the substance more thoroughly some of the oily mass was treated with a solution of baric hydrate, and the barium salt formed, which had a gelatinous consistency, was washed with cold water, dissolved in cold alcohol, from which it was allowed to crystallize, and after being dried at  $100^{\circ}$  analyzed with the following result:

0.1816 gram of the salt gave 0.0485 gram of baric sulphate.

	Calculated for (C <sub>6</sub> HBr <sub>3</sub> NO <sub>2</sub> O) <sub>2</sub> Ba.	Found.
Barium	15.45	15.70

There can be no doubt, therefore, that the phenol is tribromnitrophenol formed from tribromdinitrobenzol by the replacement of one of the nitro groups by one hydroxyl radical. Our substance also shows two characteristic properties, which have been observed in the case of the tribromnitrophenol; these are the solubility of its barium salt in alcohol, and the fact that the sodium salt is not decomposed by organic acids. The constitution of the phenol follows from its mode of formation from tribromdinitrobenzol melting at  $192^{\circ}$ . It is Br<sub>3</sub>1,3,5,OH2.NO<sub>2</sub>4.

The following statement of the yields of these various products of the action of cold sodic ethylate on tribromdinitrobenzol will give a general idea of the extent to which each of the reactions takes place, but it should be remembered that these numbers are approximate estimates rather than strict

<sup>1</sup> Ber. d. chem. Ges., 18, 1167.

determinations, as must necessarily be the case where the products are purified by crystallization. The numbers are percentages of the theoretical yield in each case:

	Per cent.
$C_6HBr(OC_2H_5)_2(NO_2)_2$ , melting-point $184^\circ$	22
$C_6HBr(OC_2H_5)_2(NO_2)_2$ , melting-point $92^\circ$	19
$C_6H(OC_2H_5)_3(NO_2)_3$ , melting-point $105^\circ$	19
$C_6H_2(OC_2H_5)OH(NO_2)_2$ , melting-point $77^\circ$	6
$C_6HBr_3(NO_2)OH$ , melting-point $90^\circ$	1
Total	67

It appears from this that the principal reaction is that which forms the bromdinitroresorcine diethylether melting at  $92^\circ$ , since the dinitrophloroglucine triethylether must be formed from this by a secondary reaction, and the yield of the two together is 38 per cent. Next after this comes the reaction forming the bromdinitroresorcine diethylether melting at  $184^\circ$ , and its decomposition-product, the dinitroresorcine monoethylether, as these together make up 28 per cent of the theoretical yield, while the third primary reaction, that which forms the tribromnitrophenol, is of very inferior importance, yielding only 1 per cent. These results also make it probable that no other product was formed in any considerable amount, as the percentage unaccounted for (33) is no greater than the loss which would be expected from such numbers of crystallizations, and other wasteful methods of purification as were necessary in isolating the substances enumerated. Small quantities of oily products were observed at various points in the work, as stated in the description of the purification, but except for these all the products were recognized.

*Constitution of the Dinitroresorcine Diethylether Melting at  $133^\circ$ .*

The dinitroresorcine diethylether was boiled for some time with sulphuric acid of specific gravity 1.44 in a flask with a return cooler. The reaction runs smoothly, and gives an almost quantitative yield of the symmetrical dinitroresorcine  $(OC_2H_5)_2$ , 1,5,  $(NO_2)_2$ , 2,4. This was recognized by its melting-point  $210^\circ$ – $211^\circ$ ; Typke<sup>1</sup> gives  $212^\circ$ .5, Schiaparelli and Abelli<sup>2</sup>

<sup>1</sup> Ber. d. chem. Ges., 16, 552.

<sup>2</sup> *Ibid.*, 16, 872.



214°.5, both of which are higher than that observed by us; but, as only two dinitroresorcines could be formed from tribromdinitrobenzol, the symmetrical one, whose melting-point is given above, and the adjacent, which melts at 142°, there can be no doubt about the identity of our substance. Many of its other properties also coincide with those given for symmetrical dinitroresorcine. It formed vitreous yellowish prisms apparently belonging to the monoclinic system when crystallized from acetic ester, but crystallized from alcohol in the spear-head forms, which were obtained by Typke from sublimation. The sodium salt was orange-red, the ammonium salt yellow prisms, the silver salt a red precipitate which soon turned brown. The acid barium salt consisted of rather thick yellow needles. We did not succeed in getting the carmine-red neutral barium salt. The free phenol decomposes carbonates.

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## THE ACTION OF SULPHOCARBANILIDE ON CERTAIN ACID ANHYDRIDES.

BY FREDERICK L. DUNLAP.

In a previous article<sup>1</sup> the results were given of a study of the action of sulphocarbaniide on the anhydrides of phthalic and succinic acids. It was found that when phthalic anhydride and sulphocarbaniide were heated, in molecular proportions, to a temperature of 125°–130°, the resulting products were phthalanilic acid and phenyl mustard oil; if the temperature, however, was raised to 170°–175°, the products were phthalanil, carbonic oxysulphide, and aniline. When equal molecular proportions of succinic anhydride and sulphocarbaniide were heated together succinanil, carbonic oxysulphide and aniline were obtained; but the formation of succinanilic acid and phenyl mustard oil (corresponding to the formation of phthalanilic acid and phenyl mustard oil) was not observed.

A further study of the action of sulphocarbaniide on succinic anhydride has, however, shown that by a correct regulation of the temperature, the formation of succinanilic acid and

<sup>1</sup> This JOURNAL, 18, 332.



phenyl mustard oil as final products, may be brought about.

*Succinanilic Acid.*—Equal molecules of succinic anhydride and sulphocarbanilide were mixed intimately by grinding together to a fine powder. This mixture was heated in a small Erlenmeyer flask placed in a Victor Meyer constant-temperature bath. The liquid in this bath was water, and during the experiment the temperature kept constant at  $95^{\circ}$ – $96^{\circ}$ . After heating the mixture of sulphocarbanilide and succinic anhydride for one and a half hours, it had begun to soften and the odor of phenyl mustard oil was plainly discernible. After three hours' heating the mixture had completely melted down. The entire length of heating was six hours. After cooling, the contents of the flask were treated with a few cubic centimeters of cold alcohol to dissolve out the phenyl mustard oil present. The residue was then treated with ammonia, and all dissolved excepting a very small amount. After filtering, hydrochloric acid threw down a white crystalline precipitate. This product crystallized from water in bunches of short prisms and, when pure, had a melting-point of  $144.5^{\circ}$ – $145.5^{\circ}$ . Menshutkin<sup>1</sup> gives the melting-point as  $138.5^{\circ}$  and Gerhardt and Laurent<sup>2</sup> as  $155^{\circ}$ .

This substance was dried at  $100^{\circ}$  and, upon analysis, gave the following results :

0.2307 gram of substance gave 15 cc. of nitrogen at  $13.6^{\circ}$  C. and 737.8 mm. pressure.

	Calculated for $C_{10}H_{11}O_3N$ .	Found.
N	7.25	7.47

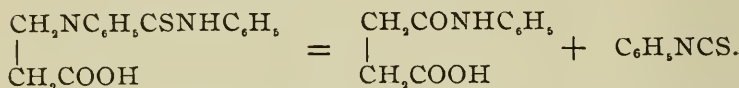
Succinanilic acid is readily soluble in acetone and alcohol, very slightly soluble in ether, and insoluble in ligroin, chloroform, benzene, and carbon bisulphide.

The preparation of succinanilic acid in this way was the outcome of a number of experiments to obtain the addition-product of succinic anhydride and sulphocarbanilide, but all of the experiments gave negative results, only the decomposition-products of this addition-product being obtained. Certainly it is highly probable that such an addition-product is formed ; but it is unquestionably very unstable, and, accord-

<sup>1</sup> Ann. Chem. (Liebig), 162, 179.

<sup>2</sup> *Ibid.*, 68, 28.

ing to the temperature of the reaction, breaks down into succin-anilic acid and phenyl mustard oil, or into succinanil, carbonic oxysulphide, and aniline.<sup>1</sup> The reaction in which succinanilic acid is formed may be explained by the following equations :



A number of experiments were also made to obtain the addition-product of phthalic anhydride and sulphocarbanilide, but these too yielded negative results. Although the temperature at which these reactions were tried was low and the time taken for the substances to combine was a number of hours, yet only the phthalanilic acid and phenyl mustard oil could be isolated.

The formation of an addition-product between the succinic or phthalic anhydride and sulphocarbanilide, although unstable and immediately giving decomposition-products, becomes highly probable on account of the isolation of a stable addition-product of maleïc anhydride and sulphocarbanilide.

*Diphenylthiomaleïnuric Acid*.—Equal molecules of maleïc anhydride and sulphocarbanilide were intimately mixed and ground to a fine powder. This mixture was heated in a small Erlenmeyer flask in an oil-bath. When the temperature of the bath was 80° the mixture began to melt. The temperature of the bath was raised gradually, and by the time the thermometer registered 95° the contents of the flask had completely melted and resolidified. This product was recrystallized from alcohol, from which it separates in bunches of short, flat, transparent prisms melting at 160°.

On analysis the following results were obtained :

0.2416 g subst. : 0.1744 g BaSO<sub>4</sub>.

0.2052 g subst. : 16.3 cc. N (27° C., 754.3 mm.).

C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>SO<sub>3</sub>. Calc. S, 9.82 ; N, 8.59.

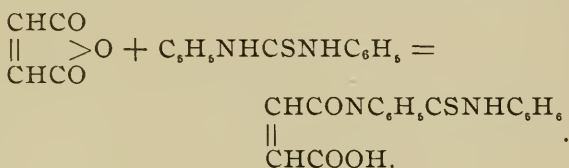
Found S, 9.91 ; N, 8.80.

<sup>1</sup> This JOURNAL, 18, 340.

Diphenylthiomaleïnuric acid is readily soluble in acetone, very sparingly soluble in ether and chloroform; insoluble in benzene, ligroin, carbon bisulphide, and water. This acid forms crystalline barium, calcium, silver, potassium, and sodium salts.

If a mixture of maleïc anhydride and sulphocarbanilide is heated in an oil-bath to 180°, a small amount of carbonic oxy-sulphide is evolved, an evolution which becomes stronger if the temperature is raised to 200° or more.

Diphenylthiomaleïnuric acid is formed by the addition of maleïc anhydride and sulphocarbanilide, as follows :



SALISBURY LABORATORIES,  
WORCESTER POLYTECHNIC INSTITUTE.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

## THE ACTION OF AMMONIA AND AMINES ON CHLORIDES OF SILICON.

BY FELIX LENGFELD.

Notwithstanding their importance and reactivity the chlorides of silicon have been little investigated. This is particularly noticeable when we consider the action of these bodies on nitrogen compounds and, more especially ammonia derivatives. Here we must expect interesting results, yet little has been done with silicon tetrachloride and even less with silicochloroform. Wöhler and Deville<sup>1</sup> obtained silicon nitride, Si<sub>3</sub>N<sub>4</sub>, by heating the product of the action of ammonia on silicon tetrachloride or silicochloroform. They paid little attention to the product before heating.

Schützenberger<sup>2</sup> also studied the action of ammonia on silicon tetrachloride. He likewise heated, in a current of hydrogen or ammonia without investigating, the bodies first formed.

<sup>1</sup> Pogg. Ann., 102, 317; Ann. Chem. (Liebig), 104, 256.

<sup>2</sup> Compt. rend., 89, 644.

Persoz<sup>1</sup> considered the white substance formed when silicon tetrachloride absorbs ammonia to be an addition-product,  $\text{SiCl}_4 \cdot 6\text{NH}_3$ .

Besson<sup>2</sup> has since confirmed Persoz's work so far as the composition is concerned.

Gattermann<sup>3</sup> obtained from silicon tetrachloride and ammonia a white powder which he considered silicon diimide,  $\text{Si}(\text{NH})_2$ , or silicocyanamide,  $\text{NSiNH}_2$ . He indicated the possibility of getting from silicochloroform and ammonia hydrosilicocyanic acid,  $\text{SiNH}$ . Gattermann gave no analysis, and so far as I can see has published nothing further on the subject.

The action of aromatic amines on silicon tetrachloride has been studied by Girard and Pabst,<sup>4</sup> Hardin,<sup>5</sup> Reynolds,<sup>6</sup> Harold,<sup>7</sup> and Combes.<sup>8</sup> Girard and Pabst worked at high temperatures and obtained the products of secondary action only. Harden obtained the compound  $\text{SiCl}_2(\text{NHC}_6\text{H}_5)_2$ , and Reynolds the compound  $\text{Si}(\text{NHC}_6\text{H}_5)_4$ , from silicon tetrachloride and aniline and similar compounds from its homologues. Harold, working in Prof. Edgar F. Smith's laboratory, has shown that the difference in results is due to a difference in conditions. He considers the chlorine-free bodies formed by the action of excess of aniline on bodies of the type  $\text{SiCl}_2(\text{NHR})_2$ . Combes obtained from parabromdimethylaniline with silicon tetrachloride the product,  $\text{Si}[\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2]_4$ , and with silicochloroform the product,  $\text{HSi}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_3$ , using sodium to remove halogen. He<sup>9</sup> also obtained from aniline and silico chloroform the compounds  $\text{HSi}(\text{NHC}_6\text{H}_5)_3$  and  $\text{HSiCl}(\text{NHC}_6\text{H}_5)_2$ .

It seemed of importance to study the reactions of the chlorides of silicon further, and especially the reactions of silicochloroform. Silicochloroform was made by the method of Gattermann<sup>10</sup> slightly modified. Adopting the suggestion of Vigouroux,<sup>11</sup> the magnesium and sand were carefully dried

<sup>1</sup> Ann. chim. phys., **44**, 419.

<sup>2</sup> Ber. d. chem. Ges., **22**, 194.

<sup>3</sup> J. Chem. Soc., **51**, 40.

<sup>4</sup> J. Am. Chem. Soc., **20**, 20.

<sup>5</sup> Compt. rend., **122**, 531.

<sup>6</sup> Ann. chim. phys. (7), **12**, 29.

<sup>7</sup> Compt. rend., **110**, 240.

<sup>8</sup> Bull. Soc. chim., **34**, 38.

<sup>9</sup> *Ibid.*, **55**, 474.

<sup>10</sup> Compt. rend., **122**, 622.

<sup>11</sup> Ber. d. chem. Ges., **22**, 190.

and but a small excess of the latter used. This greatly increases the quantity of silicon that may be put into the combustion tube, and therefore the amount of silicochloroform from each charge. A more volatile chloride than silicochloroform seems to be one of the products of the reaction. It was not isolated. It is probably  $\text{SiH}_2\text{Cl}_2$ .

I have done considerable work on silico chloroform, but before drawing any conclusions have found it necessary to study some reactions of the tetrachloride and it is with these that this preliminary paper will deal.

*Action of Ammonia on Silicon Tetrachloride.*

In order to control the quantity of ammonia it was dissolved in anhydrous benzene and mixed with silicon tetrachloride in the same solvent. During the operation the apparatus was filled with dry nitrogen, air and moisture being carefully excluded. The flocculent white precipitate formed was forced by a current of nitrogen into a large adapter, used as a funnel. The adapter was plugged at the small end with absorbent cotton so that the precipitate could be washed with benzene or ligroin. The apparatus was so arranged that the washing could be done without admitting air.

When necessary the adapter was surrounded with hot water, the filter bottle connected with the pump, and a current of nitrogen passed over the precipitate at a temperature of  $80^\circ$ – $90^\circ$  and a pressure of 25–30 mm. The precipitate caked to such an extent that even under these conditions some wash-liquor remained. This could be removed by powdering in a mortar and again drying under diminished pressure, but this operation was attended with partial decomposition by the moisture of the air. Therefore analyses were made of products containing benzene or ligroin. Ligroin was frequently used for washing, but ammonia is too little soluble in petroleum ether to permit its use as a menstruum.

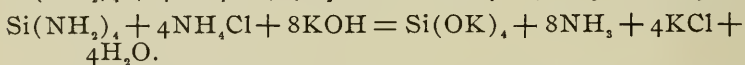
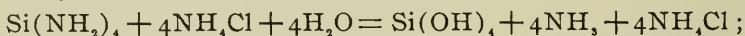
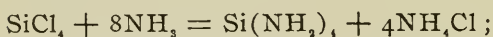
The following methods of analysis were used: Silicon was determined by treating the substance with fuming nitric acid and weighing the silicic oxide. To determine chlorine a portion was added to water, nitric acid, and silver nitrate, and allowed to stand over night. The precipitate was dissolved



in potassium cyanide and silver deposited electrolytically, or it was dissolved in ammonia, reprecipitated by nitric acid, and weighed as silver chloride. In the latter case a weighed portion was always reduced to silver to see if the silver chloride was free from silica. In every case it was pure.

Nitrogen was determined by adding water, distilling, and titrating the distillate with standard acid. The distillate was then returned to the distilling-flask, sodic hydrate added, and the ammonia again distilled and determined. From the latter titration the total nitrogen was calculated; from the former, that set free by water. The Dumas method could not be used, as ammonia came off before heating.

Seven grams (1 mol.) silicon tetrachloride was dissolved in 200 cc. benzene and to it added 5.6 grams (8 mols.) ammonia dissolved in 800 cc. benzene at 5°. After settling, 50 cc. of the clear liquid was drawn off and found to contain less than 0.25 milligram ammonia and no silicon. The action is therefore practically complete, and no soluble silicon compound is formed. The benzene was drawn off, the precipitate mixed so as to get it as nearly homogeneous as possible and an unweighed portion thrown into water. After two days the ammonia was distilled into  $\frac{N}{10}$  sulphuric acid and titrated. The ammonium sulphate was returned to the distilling flask, potassic hydrate added, and the ammonia distilled and titrated. The ammonia formed by the action of water neutralized 27.5 cc.  $\frac{N}{10}$   $H_2SO_4$ , the total ammonia required 58 cc., or twice as much. The following reactions are therefore indicated:



Silicon tetramide is a white solid. It is extremely unstable and cannot be dried, even at low temperatures, without losing ammonia and giving silicon diimide. It loses ammonia slowly at ordinary temperatures even under benzene. When ligroin is added to the fresh product, there is immediate evolution of gas and formation of silicon diimide. Silicon di-



imide,  $\text{Si}(\text{NH})_2$ ,<sup>1</sup> was obtained by Gattermann,<sup>2</sup> and probably by Persoz<sup>3</sup> and Besson.<sup>4</sup> The last two consider the product of the action of ammonia on silicon tetrachloride to be the compound  $\text{SiCl}_4\cdot 6\text{NH}_3$ . Analysis shows that not a single substance but a mixture is obtained. Unless carefully mixed the different layers do not give concordant results. This is not due to the action of moisture for if carefully mixed, different layers show no difference, even after a considerable time. The ratio of silicon to ammonia liberated by water is in different layers practically constant, while that of silicon to chlorine or to total nitrogen varies. This seems to indicate a mixture of silicon diimide and ammonium chloride in varying proportions. As the two could not be separated, analysis was made of the mixture as formed. Some freshly prepared substance was rapidly powdered and mixed in a mortar and dried for twenty-four hours in a current of nitrogen at  $85^\circ$  and 25 mm. It still contained some ligroin.

0.1202 g subst. : 0.1837 g Ag = 50.21 p c Cl.

0.2359 g subst. : 0.0489 g  $\text{SiO}_2$  = 9.75 p c Si.

0.3288 g subst. : (with  $\text{H}_2\text{O}$ ) 0.0366 g  $\text{NH}_3$  = 9.16 p c N.

0.3288 g subst. : (with KOH) 0.1139 g  $\text{NH}_3$  = 28.56 p c N.

$\text{Si}(\text{NH}_2)_4\text{NH}_4\text{Cl}$ . Calc. Si, 10.29; Cl, 52.20; N (in imide), 10.29; N (in chloride), 20.59.

Found. Si, 9.75; Cl, 50.21; N (in imide), 9.16; N (in chloride), 19.40.

The analytical results seem not to agree with the reactions indicated. They sum up to only 96 per cent of the theory. This is due to the presence of about 4 per cent ligroin. Taking this into consideration, we get :

$\text{Si}(\text{NH})_2\cdot 4\text{NH}_4\text{Cl}$ . Calc. Si, 9.88; Cl, 50.11; N (in imide), 9.88; N (in chloride), 19.77.

Found. Si, 9.75; Cl, 50.21; N (in imide), 9.16; N (in chloride), 19.40.

This leaves little doubt of the composition of the mixture.

<sup>1</sup> I shall call this body silicon diimide though it may be silicocyanamide.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Loc. cit.*

The low yield of ammonia from imide is due to the action of moisture, as this sample was powdered in the air.

It was shown by a number of analyses of carefully mixed though moist precipitate that silicon diimide is the ultimate product if water and air are excluded. One-third the total ammonia was obtained with water. Selecting two analyses at random :

I. 0.3887 g subst. gave with water 0.03825 g ammonia and with potassic hydrate 0.1139 g ammonia = 8.1 per cent and 24.13 per cent nitrogen.

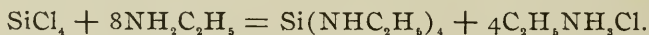
II. 0.4276 g subst. gave with water 0.04675 g ammonia, and with potassic hydrate 0.14025 g ammonia = 9.08 per cent and 27.24 per cent nitrogen.

The first action of excess of ammonia on silicon chloride in benzene is the formation of silicon tetramide and ammonium chloride. Silicon tetramide loses ammonia and gives silicon diimide, a white powder, decomposed by water, stable in the absence of moisture. It has not yet been separated from ammonium chloride, nor has its constitution been determined.

In order to prove that the action of ammonia on silicon tetrachloride is more than mere addition aliphatic amines were substituted for ammonia. The reactions of secondary amines on silicon chloride are more complicated than those of primary amines and will be treated of in a later paper.

*Action of Ethylamine on Silicon Tetrachloride. Silicon Tetrethylamine.*

Twenty grams of ethyl amine were dissolved in 400 cc. ligroin (b. p. 40°–60°) and 9 grams silicon tetrachloride in 50 cc. ligroin slowly added, the whole being cooled with ice-water. Ethyl ammonium chloride at once precipitated and was filtered from the solution. The ligroin was evaporated and the residue distilled under diminished pressure. Most of it came over at 102° under 20 mm. pressure. It contained silicon, nitrogen, carbon, and hydrogen, but no chlorine, and proved to be silicon tetrethylamine, the reaction being



The silicon was determined by weighing some of the oil in a small bulb with capillary, breaking the capillary near the end,

dipping into alcohol, and alternately heating and cooling until all the oil had been washed out. A solution of sodic hydrate was added, the mixture allowed to stand two hours, and evaporated to dryness.

The silica was then determined in the usual way.

I. 0.310 g subst. : 0.0905 g  $\text{SiO}_2$  = 13.67 p c Si.

II. 0.1812 g subst. : 44 cc. N (749 mm.,  $20^\circ.5$ ) = 27.43 pc N.

III. 0.2119 g subst. : 0.3664 g  $\text{CO}_2$ ; 0.2233 g  $\text{H}_2\text{O}$ .

$\text{Si}(\text{NHC}_2\text{H}_5)_4$ . Calc. C, 47.05; H, 11.76; N, 27.43; Si, 13.73.

Found. C, 47.14; H, 11.75; N, 27.43; Si, 13.67.

Silicon tetrethylamine is a colorless oil that does not solidify in a freezing-mixture. It keeps indefinitely in closed tubes, is decomposed by water, though not instantly, and is soluble in most organic solvents. Dilute nitric acid dissolves it without complete decomposition. It boils at  $102^\circ$  under a pressure of 20 mm.

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## NOTES.

### *The Hodgkins Medal.*

This medal was recently awarded to Professor James Dewar of the Royal Institution, by the Smithsonian Institution. In the letter accompanying the medal, Professor Langley, the Secretary, says: "It gives me great pleasure to inform you, on the part of the Institution, that the first Gold Medal of the Hodgkins Foundation has been awarded to you in recognition of your indefatigable researches pursued for so many years, which have not only been potent in increasing and diffusing a more exact knowledge in regard to the nature and properties of air, but have opened the way for a practical utilization of this knowledge in the advancement of human welfare." Mr. Hodgkins became interested in the subject of the atmosphere through the beneficial results he experienced from the air of one of the New Jersey resorts. With the idea of increasing the benefits to mankind by the scientific study of the cause of such results he specified that the income from the fund should be used in promoting a knowledge of the atmosphere. It was from this fund that Lord Rayleigh and

Professor Ramsay were awarded \$10,000 for their researches on the gases of the atmosphere.

J. E. G.

### *Liquid Air Machines.*

Another note, in the matter of the contested claims of Hampson, Linde, and Tripler as to the priority of their liquid air machines, has recently appeared, in a reply by Linde<sup>1</sup> to the statement made by Ramsay that Hampson's patent antedated that of Linde, although the principle made use of was the same in both. He calls attention to the provisional specification of Siemens, in 1857, for a combination of a cold air machine with an apparatus in which the compressed air could be cooled by the expansion of air, and to the patent granted to Solvay, in 1885, for an improvement on the principle used by Siemens. In May, 1895, Hampson, in his provisional specification, says: "The usual cycle of compression, cooling, and expansion, is modified by using all the gas after its expansion to reduce as nearly as possible to its own temperature the compressed gas which is on its way to be expanded." No mention is made of the ideas of Siemens or Solvay nor of the application of the Thomson-Joule effect. From the 20th to the 25th of May, 1895, Linde was exhibiting his machine in Munich and was making liquid air by the liter. His machine was described in the Journals in September, 1895, while it was not until April, 1896, that Hampson handed in the patent specifications, in which now the Thomson-Joule effect was given as the source of cold.

J. E. G.

### *Gases of the Argon-Helium Type.*

In a recent number of the *Berichte*<sup>2</sup>, Bohuslav Brauner contends that the position taken by the majority of chemists in accepting the gases discovered by Ramsay as elementary monatomic substances, and in attempting to find places for them in the Periodic System, is not justified by the results reached in the investigations of their nature and properties. He considers it his duty to emphasize the objections, which have been offered by himself and others, to these views, although he is almost the only one, of a number who at first hesitated to accept Ramsay's ideas, who still denies the justice of the claims. He starts out by assuming that metargon contains carbon, on account of its peculiar spectra, and as Ramsay bases his opinion of its monatomic condition on the factor 1.66 as obtained from the ratio of specific heats, he argues that this figure cannot serve as a criterion for monatomicity since it is obtained in the case of the compound gas metargon. He

<sup>1</sup> Ber. d. chem. Ges., 32, 925.

<sup>2</sup> *Ibid.*, 32, 708.

considers the inactivity of these gases another strong argument against their atomic condition, for it is generally found that substances are most active in the atomic condition. He suggests again the possibility of the atoms being so firmly and closely held together that they show no internal vibration and act as a monatomic gas. While commending the remarkable work of Ramsay, he considers that the work only justified the conclusion that he was working with extremely interesting inactive compounds or allotropic modifications of substances already known, rather than with a series of new elements. He also quotes a recent paper by Piccini<sup>1</sup> in support of his view. In this paper the author contends that there is no place in the Periodic System for the new gases, where their position and properties can be reconciled, nor are the atomic volumes or boiling-points what they should be to conform to the generalizations as expressed in the curves of atomic volumes and of boiling-points.

J. E. G.

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### REVIEWS.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492-1897. By H. CARRINGTON BOLTON. First Supplement. Smithsonian Institute. 1899.

In 1893 Professor Bolton published a bibliography of chemistry which contained about 12,000 titles, under the following heads: Bibliography, Dictionaries and Tables, History of Chemistry, Biography, Chemistry, Pure and Applied, and Periodicals. In this supplementary volume he has added more than 5,000 titles of books published since 1893, or before unknown. Professor Bolton has a special fondness for the historical and bibliographical side of chemistry, and has published a number of papers of his researches in these lines, a kind of work which is very desirable and necessary and for which comparatively few have the patience and systematic habits. Besides his own researches carried on in the libraries abroad and in this country, the author had the cooperation of a number of chemists who supplied lists of the publications of their respective countries.

J. E. G.

THE FREE EXPANSION OF GASES. Translated and edited by J. S. AMES, PH.D., Professor of Physics in Johns Hopkins University. 75 cents.

PRISMATIC AND DIFFRACTION SPECTRA. Translated and edited by J. S. AMES, PH.D. 60 cents.

RÖNTGEN RAYS. Translated and edited by GEORGE F. BARKER, I.L.D., Professor of Physics in the University of Pennsylvania. 60 cents.

THE MODERN THEORY OF SOLUTION. Translated and edited by HARRY C. JONES, PH.D., Associate in Physical Chemistry in Johns Hopkins University. \$1.00 Harper & Brothers, New York and London. 1898.

An idea of the general field which this series, edited by

<sup>1</sup> Ztschr. anorg. Chem., 19, 295.



Joseph S. Ames, Ph.D., Professor of Physics in Johns Hopkins University, is expected to cover, can perhaps be best obtained from extracts from announcements of the publishers.

"This series will embrace a large number of translations and reprints of the most important articles which have been written in the history of science, including many which have an important bearing upon the present state of science. The fields of physics, astronomy, chemistry, and probably other sciences will be covered." "This series will lay before the general reader the original statements of many of the more important theories and experiments which until now have not been readily accessible."

Many of the original papers, published by the chemists of the last century and the early part of this one, which contain results upon which the present theories of chemistry are founded, have been rendered accessible to everyone through the efforts of Professor Ostwald, who has edited reprints of a number of these papers under the general title "*Ostwald's Klassiker der exakten Wissenschaften*." In a similar series published in England under the title "*Alembic Club Reprints*," we find a number of the most important articles that were published in English journals, such as those of Davy, Dalton, Faraday, and Priestley.

In this present series, as stated in the announcement, more than one science is to be included, though the volumes so far announced only include those in the field of physics and physical chemistry. In the first three volumes, which have already come to hand, we have the important papers by the following authors: in the first by Gay-Lussac, Joule and Thomson; in the second by Fraunhofer; and in the third by Röntgen, Stokes and Thomson. These numbers also contain notes by the editors and biographical sketches and bibliographies. In the volume on "*The Modern Theories of Solution*," in which the chemist is more especially interested, we find translations of the papers which are the foundation stones of the present theories of physical chemistry and which have bridged the chasm between the domain of the physicist and that of the chemist. In it we find the articles by Pfeffer on "*Osmotic Investigations*," by Van't Hoff on "*Osmotic Pressure*," by Arrhenius on "*Dissociation of Substances Dissolved in Water*," by Raoult on "*The General Law of the Freezing of Solvents*," "*On the Vapor-Pressure of Ethereal Solutions*," and "*The General Law of the Vapor-Pressure of Solvents*." The value of these articles is further increased by the general review of their influence on the development of the science and by the valuable



bibliography covering the subjects of Osmotic Pressure, Theory of Solution and Changes in Freezing-Point and Boiling-Point caused by Dissolved Substances. No one can fail to recognize the great importance of a knowledge of the work of others as acquired from a study of these original records, to enable one to get in touch with the writer and to see with his eyes and hear with his ears so far as possible, instead of through the biased or misstated records of opponents or competitors. These volumes are published in a very neat and attractive form and can be recommended as valuable supplements to text-books on the subjects treated of in this series.

J. E. G.

TRAITÉ D'ANALYSE CHIMIQUE QUANTITATIVE PAR ELECTROLYSE. By J. RIBAN, (Paris). [Masson et Cie. 1899. pp. VI, 304].

Since Gibbs and Luckow first used electrolysis as a means of quantitative determination thirty-five years ago, this application of electricity has steadily risen in favor. Many eminent chemists have given time and thought to the detailed study of special cases, and it is pleasant to see that Professor Riban is familiar with a wide range of this literature. The works of Classen, Smith, Neumann, Riche, Freudenberg, and others are freely quoted in the book under discussion, without however giving either reference or date. The omission is much to be deplored, but its detrimental effect is somewhat diminished by the very full re-statement of the methods and data. Indeed the repetition frequently leads the author into masses of unessentials which somewhat encumber the main thread of the argument.

The book is divided into four parts, of which the first recounts the physical laws underlying the practice of electrolysis, as well as the apparatus necessary to produce and to utilize galvanic energy. Some of the description is particularly clear and to the point, but it is not free from occasional error. The most incomprehensible mistake is the adherence to the old idea that the total heat of a reaction is convertible into electrical energy, in spite of the fact that M. Riban has evidently seen the equation of Helmholtz. A recent description of the theory of electrolytic separation with no allusion to the illuminating hypotheses of Arrhenius and of Nernst is indeed an oddity, but it is to be encountered here. On the practical side the book is much more trustworthy, recommending the dynamo and accumulator as usually the most convenient fountain of energy, and describing in minute detail every conceivable form of anode and kathode. While most of the connections recommended are good, the switch-board pictured on page 126 is a tempting invitation to a short-circuit, that sub-

tle trap always waiting for the uninitiated. The gas-“ voltmeter” is scarcely condemned in strong enough language, and the grave inconvenience involved in the use of a series-dynamo for charging cells might be emphasized more trenchantly.

It is unfortunate that most writers upon electrolytic analysis, M. Riban among the rest, dwell upon the accidental voltage existing between the electrodes while the current is running as an important factor in the case. This voltage is of course made up of two quantities, the normal fall of potential due to the unknown resistance of the solution, and the “polarization” of the cell. The polarization is really the essential question; it varies with the metal to be deposited, and is the only sure criterion for determining what substances are to appear in the elementary state. If the resistance and current strength were known, the polarization could of course be calculated with ease, from the total potential registered by a voltmeter; but the analyst does not usually have any knowledge of the ever-changing resistance in his cell. Hence the determination of the “Klemmspannung” is rather an idle sport. The plan, so much condemned by Classen, Riban, and others, of using as the source of current a galvanic cell with a potential between those of the polarizations corresponding to two metals to be separated is really a safer one, if the electrolysis is to run without constant supervision.

The three remaining parts of the book treat of individual determinations, of separations, and of technical applications respectively. One is glad to find that the author, besides recounting most of the methods which have been proposed, sometimes criticises them upon the basis of his own experience. A still rarer virtue is to be found in the occasional advice to use ordinary gravimetric methods rather than electrolytic; for enthusiasm about the frequent real advantages of electrolysis sometimes leads chemists to apply electrolytic methods to cases better treated in other ways.

During the perusal of this detailed part of the book one asks one's self continually the question “Why?” In fact, very many problems remain still to be studied concerning the mechanism of deposition in complex solutions, but M. Riban has by no means explained all which now seem explicable. For instance, he has failed to call attention to Foerster's admirable explanation of the deposition of cuprous oxide from neutral solutions of cupric sulphate. The chapter dealing with technical applications occupies only 29 pages and is very incomplete. The presswork and illustrations are in characteristically admirable French style.

In short, this volume is not an unmixed success; and while

in France it may take the place of the works of Neumann, Classen and Smith, it will not be likely to supplant them in the laboratories of America, England, and Germany. As a record of evident practical experience with many of the methods it is distinctly of value.

T. W. R.

EXAMINATION OF WATER (CHEMICAL AND BACTERIOLOGICAL). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 135. 1899.

A useful practical manual of water examination for sanitary purposes, in which not only the methods for making the several determinations are explained at length, but general remarks, sensible and well balanced, are made on the interpretation of these determinations, the relative importance to be attached to them, and the collateral facts to be weighed in connection with them. Various special cases occurring in the experience of the author are referred to, which are interesting and instructive, for example, on p. 47, the finding an unusually large amount of nitrates in the water of a deep rock-drilled well, traced to the fact of fifty pounds of nitroglycerine having been used to "torpedo" the well.

It might perhaps have been well, in the second part of the manual, to have given a little more of general matter on bacteria and their relations to health and disease, and to have insisted a little more strenuously on the very special precautions necessary in the collection, preservation, and transport of water samples, to render a bacteriological examination of any value.

J. W. M.

DAS LEITVERMÖGEN DER ELEKTROLYTE, INSBESONDERE DER LÖSUNGEN, METHODEN, RESULTATE, UND CHEMISCHE ANWENDUNGEN. VON DR. F. KOHLRAUSCH, Präsident der physikalisch-technischen Reichsanstalt, und Dr. L. HOLBORN, Mitglied der physikalisch-technischen Reichsanstalt. Mit in den Text gedruckten Figuren und einer Tafel. Leipzig: Druck und Verlag von B. G. Teubner. 1898. pp. 211.

We are especially fortunate in having a work on "conductivity," from the same hand which devised the method for determining the power of solutions of electrolytes to conduct the current. The book deals with the subject in a broad way, and contains just such information as is needed by every one who would make conductivity measurements. Chapters are devoted to: instruments and methods of measuring conductivity; methods, using the alternating current; solutions; temperature; and chemical applications of the conductivity of aqueous solutions. A complete bibliography of the literature on conductivity of electrolytes, is followed by tables of results obtained.

The discussion of the forms of apparatus which can be employed is well illustrated by drawings, and the more common sources of error in measuring conductivity with the alternating current, are pointed out in detail. The results given, are referred to a common standard of resistance, that of a cube of the substance whose edge is 1 cm. long, and are therefore directly comparable. The work is, as we should expect from its authors, beyond criticism, and cannot be commended too heartily to all who are interested in conductivity work.

H. C. J.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE. LIEBIG UND KOPP. Für 1892. Viertes Heft.

This is the last part of the first volume for 1892 and contains the table of contents. It covers the field of general, physical, and inorganic chemistry, and a part of organic.

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